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LONDON: GURNEY AND JACKSON
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Printed in Great Britain by Richard Clay & Sons, Ltd.
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after drying the solution with potassium carbonate, under diminished pressure at room temperature. This course is necessary since the base decomposes when heated in chloroform solution. This base crystallises from acetone in canary-yellow, prismatic needles, m. p. 193—194° (corr.), which are insoluble in water, fairly readily soluble in acetone or chloroform, more readily soluble in alcohol, but sparingly soluble in ether (Found: C, 79·0, 78·6; H, 6·0, 6·1. $C_{18}H_{17}N_3$ requires C, 78·6; H, 6·2%).

Iodide B crystallises from alcohol in colourless needles, m. p. 182—183° (corr.), which are anhydrous and moderately soluble in hot alcohol, but sparingly soluble in water, acetone or cold alcohol (Found: C, 64·5, 64·2, 64·0, 63·2; H, 5·4, 5·4, 5·4, 5·2; N, 13·1, 13·5; I, 19·9, 20·0. $C_{17}H_{15}N_3,C_{19}H_{20}N_3I$ requires C, 63·7; H, 5·2; N, 12·4; I, 18·7%). It proved to be a compound of 2-phenyl-6-methyl-4-anilinopyrimidine and 2-phenyl-3 : 6 (or 1 : 6)-dimethyl-4-methylanilinopyrimidinium iodide in equimolecular proportions, and was prepared synthetically by crystallising equimolecular proportions of these compounds from alcohol, the specimen so obtained having m. p. 182—183° (corr.) alone or mixed with iodide B. When iodide B (0·385 g.) was digested with silver chloride and hot water for many hours and the product filtered, the insoluble matter gave on extraction with ether 0·148 g. of 2-phenyl-6-methyl-4-anilinopyrimidine as base (m. p. 159—160°, alone or mixed with a known specimen); the filtrate when basified gave only a trace of material to ether.

2-Phenyl-6-methyl-4-methylanilinopyrimidine (VII) was prepared from 2-phenyl-6-methyl-4-chloropyrimidine and methylaniline, in the same way as the anilino-base, in practically theoretical yield. It melted at 113° (corr.) (Wheeler gives 113°). The *hydrogen oxalate* crystallises from alcohol, in which it is fairly readily soluble, in small, colourless prisms, m. p. 182—183° (decomp.; corr.) (Found: C, 66·0; H, 5·1. $C_{18}H_{17}N_3,C_2H_2O_4$ requires C, 65·8; H, 5·2%). The *picrate* crystallises from alcohol in long, yellow needles, m. p. 174—175° (corr.). It is sparingly soluble in water and fairly readily soluble in alcohol (Found: N, 16·9. $C_{18}H_{17}N_3,C_6H_3O_7N_3$ requires N, 16·7%).

4-Methylanilino-2-phenyl-3 : 6 (or 1 : 6)*-dimethylpyrimidinium iodide* (X, *a* or *b*) was prepared both from 2-phenyl-3 : 6 (or 1 : 6)-dimethyl-4-phenylimino-3 : 4-dihydropyrimidine and from 2-phenyl-6-methyl-4-methylanilinopyrimidine by heating with excess of methyl iodide for 8 hours at 100°, the respective yields of pure salt isolated being 76 and 48% of the theoretical. The pure salt from either source and a mixture of the two specimens had m. p. 215° (decomp.; corr.). It crystallised from acetone in colourless

anhydrous, prismatic needles. It is sparingly soluble in water, readily in alcohol, and fairly readily in acetone [Found (in salt from IX): I, 30·3; (in salt from VII): I, 30·5. $C_{19}H_{20}N_3I$ requires I, 30·5%].

Demethylation. The above salt, prepared from (IX), (0·5 g.) was heated to its m. p. under 15 mm. pressure, methyl iodide being thus removed. On crystallisation of the residue from acetone, 2-phenyl-6-methyl-4-methylanilinopyrimidine, m. p. 113°, was obtained, and recognised by the mixed melting-point method; yield 0·2 g., 60%.

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UNIVERSITY OF MANCHESTER. [*Received, August 11th*, 1926.]

CCCXXX.—*The Determination of the Atomic Weight of Silver by the Direct Ratio of Silver to Oxygen in Silver Oxide.*

By HARRY LISTER RILEY and HERBERT BRERETON BAKER.

1. *The Stability of Silver Oxide.*

THERE is considerable difference of opinion as to the stability of silver oxide. According to Rose (*Pogg. Ann.*, 1852, **85**, 314; *Chem. Gazz.*, 1852, **10**, 182), silver oxide decomposes in light at the ordinary temperature and suffers slight loss of oxygen at 100°. He advises 80° as the maximum temperature at which it is safe to dry the substance. Carey Lea (*Amer. J. Sci.*, 1892, **43**, 249) dried silver oxide to constant weight at 160—165°; the product had lost a small amount of oxygen. From the colour of the chloride obtained by dissolving the oxide in hydrochloric acid, he assumed that even drying at the ordinary temperature causes slight decomposition. The silver oxide, even after drying for 20 hours at 100°, still contained about 0·5% of moisture. Colson (*Compt. rend.*, 1898, **127**, 961; 1900, **130**, 330) states that the temperature can be taken to 200° without decomposition of the silver oxide. None of these workers, however, collected the oxygen evolved, their conclusions being drawn from the percentage loss in weight of the substance on ignition.

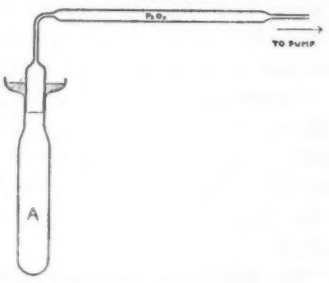
The reaction $2Ag_2O \rightleftarrows 4Ag + O_2$ has been shown by le Chatelier (*Bull. Soc. chim.*, 1887, **48**, 342; *Z. physikal. Chem.*, 1887, **1**, 516) and Lewis (*ibid.*, 1905, **52**, 310) to be reversible. The latter (*J. Amer. Chem. Soc.*, 1906, **28**, 139) measured the decomposition pressures of silver oxide (dried at 240°) at 302°, 325°, and 445° and found them to be 20·5, 32, and 204 atm. respectively. From these results he calculated the decomposition pressure of the oxide at 25° to be

5×10^{-4} atm. or approximately 0·4 mm. Hg. If this value be correct, it should be possible to dry silver oxide at the ordinary temperature and pressure without any fear of decomposition.

Madsen (*Z. anorg. Chem.*, 1913, **79**, 200) concludes that it is impossible to remove all the water from silver oxide without slight decomposition. Von Kohlschütter and Eydmann (*Annalen*, 1913, **398**, 1) report very slow decomposition at 300°. Mixter (*Amer. J. Sci.*, 1911, **32**, 202) dried silver oxide at 280°; the sample obtained, which was slightly carbonated, on analysis, showed 92% Ag (Ag_2O requires 93·1%). Hardin (*J. Amer. Chem. Soc.*, 1896, **18**, 994) mentions an attempt to determine the ratio of silver to oxygen in silver oxide, but he abandoned the experiments owing to loss of oxygen on drying the oxide.

The importance of the atomic weight of silver renders it highly desirable that it should be determined by a direct ratio of silver to oxygen in silver oxide. The ratio is not ideal, being of the order 13·5 : 1, but this disadvantage would be outweighed by the simplicity of the experimental determination of the ratio if it were possible to prepare silver oxide in the pure condition. It was therefore decided to re-investigate its stability.

FIG. 1.



Freshly-prepared silver oxide was placed in the silica tube A (Fig. 1) and the apparatus was quickly evacuated with a Fleuss pump followed by a Sprengel pump. The gas extracted by the Sprengel pump was analysed (CO_2, 0·045 c.c.; O_2, 0·020 c.c.; N_2, 0·080 c.c.) and deemed to be a mixture of carbon dioxide and air. The apparatus was then kept for 4 days to allow the oxide to dry. No depression of the mercury in the pump manometer was noticed, but on starting the pump a very small quantity of gas, about 0·01 c.c., too small for separate analysis, was collected. The tube containing the oxide was therefore immersed in a water-bath at 100° and kept at that temperature for 5 days and nights. The gas pumped off after this time was analysed, with the following result: CO_2, 0·073 c.c.; O_2, 0·008 c.c.; N_2, 0·037 c.c. Thus at 100° the gas evolved was mainly carbon dioxide, the remainder being a little air, probably from the walls of the tube. The pump was again started and kept working for a further period of 7 hours, the silica tube and contents being kept at 100°. A small bubble of gas collected which was completely absorbed by caustic potash and was therefore free from oxygen.

During the drying at the ordinary temperature, the oxide was exposed to diffused daylight, yet the oxygen and nitrogen found in the gas pumped out of the apparatus were in the ratio normally obtaining in air, thus showing that there was no excess of oxygen. Hence it seems that, contrary to previous statements, silver oxide is not decomposed to any appreciable extent by light or by drying over phosphorus pentoxide at the ordinary temperature. Moreover, since no oxygen was evolved at 100°, in a vacuum, it should be possible to dry silver oxide at 100° without any fear of decomposition. To make sure that the phosphorus pentoxide (prepared by a method described later) was not absorbing any oxygen, dry carbon dioxide-free air was admitted into the apparatus. No alteration in pressure was observed after 3 days.

The moist silver oxide placed in the apparatus, on treatment with dilute hydrochloric acid, gave a perfectly white chloride, but the chloride obtained from the oxide after drying was brownish-pink. Carey Lea (*loc. cit.*) states that this pink chloride is the photochloride. If so, then the above experiment indicated that it was formed with very slight loss of oxygen.

Experiments carried out in a similar manner at higher temperatures showed that silver oxide decomposed extremely slowly at 165°. It was also found possible to heat the oxide for several hours at 250° without any oxygen being evolved. Once the decomposition had started, however, it accelerated and soon became fairly rapid.

The above experiments indicated that it was possible to dry silver oxide over pure phosphorus pentoxide at the ordinary temperature or in a vacuum at 100° without the loss of any appreciable amount of oxygen. It seemed, however, that some very small amount of oxygen was lost, because the dried oxide always gave a pink chloride on treatment with hydrochloric acid. The pink chloride was not the photochloride as stated by Carey Lea, because experiments showed that light had nothing to do with its production. Silver oxide prepared and dried in absolute darkness also gave this pink chloride. It was thought, nevertheless, that the pink colour of the chloride might be due to a negligible loss of oxygen from the oxide and it was therefore decided to prepare silver oxide as pure as possible and analyse it with " atomic weight " accuracy.

Preparation of Pure Materials.

Water. The water used was prepared by distilling ordinary laboratory distilled water from a weakly alkaline (potassium hydroxide) solution of potassium permanganate in a copper still, through a block-copper condenser. After simmering over-night, the middle

portion of each distillate was collected in resistance glass bottles (Durosil) after the distillate had been shown to be free from ammonium compounds.

Nitric acid. Ordinary pure nitric acid (Hopkin and Williams) was distilled over silver nitrate and potassium nitrate in a Jena glass retort, and the distillate discarded until free from halogen. This acid was finally transferred to a platinum still, the middle portion of the distillate from the platinum being used. The acid was always distilled immediately before use into a small platinum flask. The strength of the acid so obtained, as determined by its density, is about 65%, this being the composition of the constant-boiling mixture.

Silver nitrate. Silver nitrate was recrystallised five times from acid solution, the crystals being dried on a porcelain centrifuge. After the fifth recrystallisation the nitrate was dissolved in water and reduced with a slight excess of pure ammonium formate, freshly prepared. When the violent ebullition and evolution of gas had subsided the spongy grey silver was broken up with a glass rod and then washed repeatedly with hot water until free from ammonia. The finely powdered amorphous silver was finally dissolved in a slight excess of freshly distilled nitric acid and crystallised once more.

All crystallisations were carried out in Austrian hard-glass vessels. Conductivity water was used throughout. In order to avoid waste of silver nitrate and also to promote quicker crystallisation, thereby reducing occlusion, the silver nitrate solution was evaporated to an oily consistency and then excess of pure nitric acid was added with continual stirring until no more crystals of silver nitrate were thrown down. In this way, each crystallisation could be carried out with a loss of 8% of nitrate.

It was found impossible to test the wash-water from the silver directly with Nessler's reagent, as the dissolved silver was sufficient to give a yellow coloration, due to the formation of silver iodide. When testing, therefore, the wash-liquors were boiled with caustic potash and the distillate was tested with Nessler's reagent. An all-glass distillation apparatus was employed. The process of washing took 2—3 days.

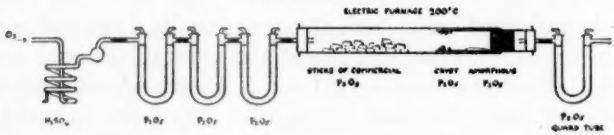
Ammonium formate. Kahlbaum's pure formic acid (d 1·2) was distilled in platinum and neutralised with ammonia, freshly prepared by boiling the concentrated solution (d 0·880) and leading the gas into conductivity water. The solution was tested for halogens by first neutralising it with pure nitric acid and then adding silver nitrate solution.

Baryta. To avoid the presence of silica, crystallisations were carried out in a pure silver flask and a large pure silver basin. One

pound of baryta (Hopkin and Williams's "pure recrystallised") was dissolved in 200 c.c. of distilled water contained in the silver flask, the flask being gently heated to effect solution. The solution was poured into the silver basin, which was surrounded by cold water and protected from dust. The finely crystalline baryta so formed was centrifuged and the crystals were damped with distilled water, recentrifuged, and again damped and centrifuged. The recrystallisation was repeated three times, after which conductivity water was used. Nine crystallisations were necessary. The baryta was then free from chloride but contained a little carbonate, which was subsequently removed.

Phosphorus pentoxide. Pellets of "pure" phosphorus pentoxide were distilled at a low temperature (180—210°) in a slow stream of oxygen, the apparatus shown in Fig. 2 being employed. The product, which consisted of fairly large crystals and a finely-divided powder, was stored in a stoppered bottle in a desiccator over phosphorus pentoxide. Owing to the unavoidable formation of the

FIG. 2.



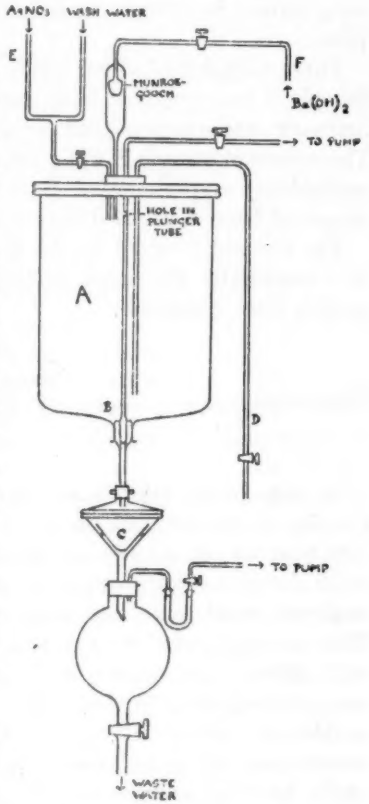
vitreous variety on the surface of the crude pentoxide, not more than 10% distilled over.

Silver oxide. An attempt to prepare pure silver oxide was made in the apparatus shown in Fig. 3. It consists of a large inverted bell-jar, A, which, by raising the plunger, B, may be put in communication with the filter C. The bell-jar is closed with a ground glass plate held firmly in position by means of wooden clamps. The glass plate is bored centrally and carries a large rubber stopper through which pass the plunger, a syphon tube, and tubes to permit the entry of silver nitrate and baryta solutions and wash-water. The lower part of the apparatus consists of a funnel and ground glass cover, held firmly together by means of a wooden clamp. The lower part of the funnel is connected to a large tap-funnel.

The preparation of silver oxide in this apparatus was carried out as follows: All parts of the apparatus were thoroughly cleaned with a mixture of chromic and nitric acids. The apparatus was then assembled, all rubber stoppers being protected by means of paraffin wax. The precipitation vessel A was completely filled with filtered distilled water and after standing over-night was emptied by means of the syphon tube D. The process was repeated with distilled water

and then with conductivity water. A current of carbon dioxide-free air was drawn through the apparatus by way of E and D until the issuing air, on bubbling through baryta solution for 6 hours, gave no precipitate. This required about 80 hours. Conductivity water was freed from carbon dioxide by bubbling a current of carbon dioxide-free air through it for 3 days at the rate of three bubbles a second.

FIG. 3.



In carrying out the precipitation a slight excess of silver nitrate was used to minimise any risk of the introduction of silica through the action of the alkaline baryta on the glass. A quantity of silver nitrate, sufficient to form about 70 g. of silver oxide, was dissolved in boiled-out conductivity water, drawn over into the precipitation vessel by way of E, and diluted to 2 litres. The equivalent quantity of pure baryta was dissolved in 2 litres of conductivity water in a silver soup tureen and drawn over into the precipitation vessel by way of F. Before entering A the baryta solution passed through a Munroe-Gooch platinum crucible sealed directly on to the glass syphon tube, all traces of carbonate being thus removed.

The precipitated silver oxide was allowed to settle over-night and the supernatant liquid decanted off through the syphon tube D. The precipitate was washed by decantation until the wash-liquors gave no turbidity with dilute sulphuric acid. It was then transferred completely to the filter. This consists of a pure silver cone with a perforated bottom. To the bottom of the cone are firmly clamped, by means of a small silver nut and bolt, two discs of pure silver gauze and a perforated silver plate. This device was quite efficient in filtering the rather coarse granular precipitate of silver oxide.

The precipitate was washed several times on the filter until free

from barium, and a current of carbon dioxide-free air was drawn through it to remove as much water as possible. The filter and precipitate were then quickly transferred to a desiccator containing solid caustic potash. After a fortnight the oxide was sufficiently dry to permit rough powdering. The drying was continued in a desiccator over pure phosphorus pentoxide for a further month. It was deemed advisable not to accelerate the drying by raising the temperature in order to make quite sure that no loss of oxygen took place.

Three samples of silver oxide were prepared, each of 60—70 g. Sample A was prepared from pure silver oxide made during the preliminary experiments and subsequently converted into nitrate. The source of sample B was pure silver nitrate, also made during the preliminary experiments. Sample C was made from the nitrate prepared from 8 oz. of Johnson and Matthey's purest assay silver.

The method adopted for the analysis of the three samples of oxide was essentially the same as that described later. The following results were obtained:

	Ratio O : Ag.		
	Sample A.	Sample B.	Sample C.
Experiment 1.....	8 : 108·08	8 : 108·64	
„ 2.....	8 : 108·07	8 : 108·64	8 : 108·03
„ 3.....	8 : 108·08	8 : 108·71	8 : 108·08

In spite of the fairly good agreement of the results of the A and C series of experiments, the great divergence of the B results and the fact that all the results are considerably higher than the accepted value for the atomic weight of silver indicated that the compound analysed must have lost some oxygen during the drying process. This was supported by the fact that all samples, on being treated with dilute hydrochloric acid, gave a pink chloride. This result was contradictory to that obtained in the preliminary experiments on the stability of the oxide. A careful repetition of these experiments gave the same result, *viz.*, that it was possible to heat silver oxide for long periods at 100° without being able to detect any oxygen in the gases pumped out of the apparatus containing the oxide.

The gravimetric results indicated that some slow reaction was taking place during the drying process which resulted in a small amount of reduction. In order to find if it were possible to speed up this reaction and also the extent to which the reduction would go, it was decided to dry the oxide at a higher temperature and then analyse the product gravimetrically. Air from a compressed-air cylinder, after bubbling through phosphoric acid and passing through a tube 4 feet long, half of which was packed with solid caustic

soda and half with phosphorus pentoxide, passed into a hard-glass tube heated electrically at 80°, containing a porcelain boat filled with freshly-prepared silver oxide. After the air had passed over the oxide for 5 days and nights, small white specks of metallic silver were observed on the oxide nearest the air inlet. After a further week, the half of the oxide nearer the inlet had become perfectly white, but the other half was still black. On taking the boat out of the tube it was found that only a very thin surface film of the oxide had been reduced, the remainder being quite black. This suggested that the reduction of the silver oxide was not due to any instability of the oxide, but that it was being reduced by the small amount of organic matter which passed through the drying tubes. A tube containing copper oxide, heated electrically to dull redness, was inserted between the compressed-air cylinder and the bubbler and the experiment repeated. No visible reduction took place during a fortnight. The temperature was raised to 120°; after a further week no white specks of metallic silver had appeared.

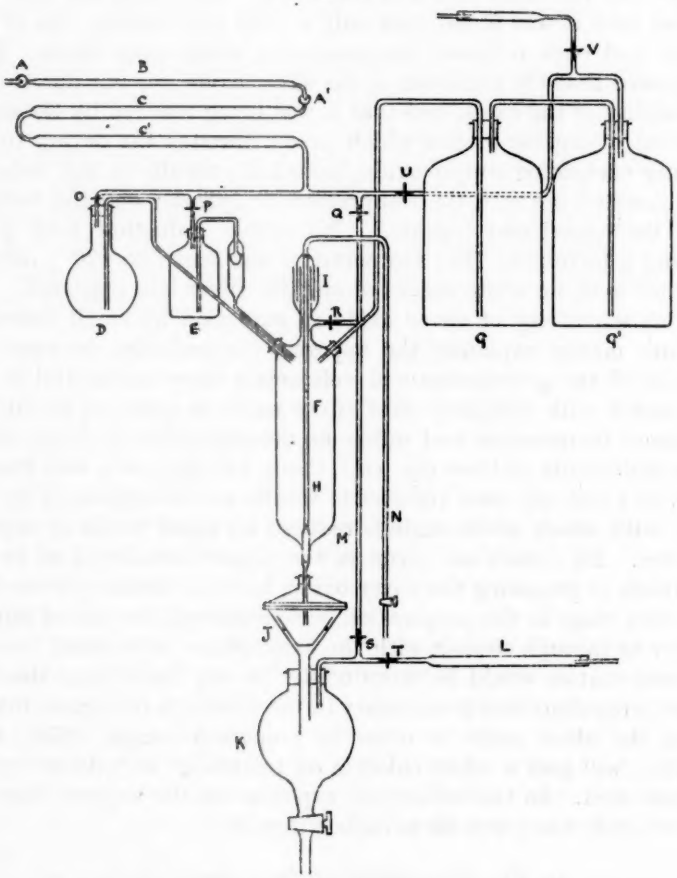
This sensitivity of silver oxide to reduction by small traces of organic matter explained the apparent contradiction between the results of the gravimetric and volumetric experiments and it can be stated with certainty that silver oxide is quite stable at the ordinary temperature and suffers no decomposition on being dried. The statements of Rose (*loc. cit.*), Carey Lea (*loc. cit.*), and Hardin (*loc. cit.*) and our own volumetric results are all explained by the ease with which silver oxide is reduced by small traces of organic matter. No details are given in the papers mentioned as to the methods of preparing the silver oxide, but it is almost certain that at some stage in the preparation, either through the use of impure water or through contact with the atmosphere, some small trace of organic matter would be introduced. It was found later that the most scrupulous care is necessary in the exclusion of organic matter from the silver oxide in order to prepare a sample which, after drying, will give a white chloride on treatment with dilute hydrochloric acid. In the volumetric experiments the oxygen from the silver oxide was given off as carbon dioxide.

2. *The Preparation of Pure Silver Oxide.*

From the foregoing it will be seen that in order to prepare silver oxide of atomic weight purity, an apparatus is necessary in which precipitation, washing, and filtration can be carried out in an atmosphere entirely free from organic matter and the slightest trace of carbon dioxide. With this object in view, the apparatus shown in Fig. 4 was erected. A, B, and C constitute a system of purification tubes. A and A′ are bubblers containing syrupy phosphoric

acid. A is connected to a hard glass tube, B, by means of a piece of rubber pressure tubing. B is filled with copper oxide and may be heated electrically to dull redness. The other end of B is connected by tubing to another bubbler, A′, which is sealed on to the soda-lime tube, C. C is sealed on to another similar tube, C′, which

FIG. 4.



is half filled with soda-lime and half with purified, strongly ignited asbestos. Each of the three tubes is about 18 inches long; C and C′ are 1 inch in diameter and B ½ inch. The bubbler A is connected by means of a piece of pressure tubing to a compressed-air cylinder, the flow of air from the cylinder being regulated by an "Endurance" valve. C′ connects through a four-way piece of glass tubing with the silver nitrate vessel, D, the baryta vessel, E, the precipitation

vessel, F, and the water bottles, G and G′. Connexion is made with each of these by means of a piece of pressure tubing carrying a screw clip, so that any one of them singly may be put into communication with the supply of pure air. The silver nitrate vessel, D, is a litre Jena-glass flask fitted with a syphon tube which communicates with the precipitation vessel. The baryta vessel, E, is a pure silver flask of about 800 c.c. capacity. This also is fitted with a syphon tube, which carries a filter. The filter is a Munroe-Gooch platinum crucible sealed directly to the glass syphon tube and serves to filter the baryta solution immediately before entering the precipitation vessel. The wash-bottles are of Durosil resistance glass, each of about 10 litres capacity. Each is fitted with syphon tubes whereby G′ communicates with G and G with the precipitation vessel. The syphon tubes enter the precipitation vessel through rubber stoppers fitted in two tubuli in the upper part of F. The precipitation vessel is of about 2½ litres capacity and is of Durosil resistance glass. The lower tubulus of F is closed by a ground glass plunger. The mercury-water seal, I, permits the plunger to be raised without admitting air, so that the precipitation vessel may be put into communication with the filter funnel, J. This consists of a glass funnel and ground glass top held together by a wooden clamp. The funnel stem passes through a rubber stopper in the tubulus of the large separating funnel, K. Resting on a rubber ring in the filter funnel is the silver filter previously described. The large 2-litre separating funnel, K, may be put in communication with the atmosphere through the soda-lime guard-tube, L, or with the supply of pure air by means of the tube M.

About 2 cm. from the bottom of the plunger-tube H is a small hole so that liquid may be syphoned out of the precipitation vessel by way of the tube N.

The procedure in preparing pure silver oxide by means of this apparatus was as follows: All glass parts of the apparatus were thoroughly cleaned, first with ordinary water, followed by strong sodium hydroxide solution, distilled water, chromic and nitric acids, strong nitric acid, distilled water, and finally conductivity water. Whilst the cleaning and erection were in progress the two wash-bottles were filled directly from the still with conductivity water. As soon as they were full, the bottles were placed in position and quickly connected with the rest of the apparatus, the water being exposed to the atmosphere for only 2 or 3 seconds. With the screw clips O, P, R, V, and Q open, and S, T, and U closed, the "Endurance" pressure regulator on the compressed-air cylinder was opened so that a slow stream of purified air passed by way of the purifying tubes, through D, E, and F, and bubbled through the

water in G and G′, passing out of the apparatus by way of the soda-lime guard-tube at V. In this way it was possible to remove the last trace of carbon dioxide present in the wash-water and at the same time any introduction of organic matter into the conductivity water was avoided. After the air had been bubbling through the water for 3 days and nights it was found to be free from carbon dioxide by bubbling the issuing air through baryta solution for 6 hours, after which time no turbidity had developed.

The screw slips O, P, Q, and V were then closed and U was opened. Water was forced from G′ into G and from G into F. As soon as the syphon had started, the supply of air was cut off and Q and R were opened. Under these conditions the syphon continues to function. When F was almost full of water, U was closed and the supply of air turned on, thus immediately stopping the syphon. The plunger tube was then raised slightly and, with a slow stream of air passing into F by way of Q and R, the water was allowed to trickle through the filter into K, the air in K being driven out through the guard-tube, L. When K was full the remainder of the water was drawn off through the syphon, N. The water in K was withdrawn slowly, pure air entering *via* Q and S, and T being closed. The apparatus was now filled with pure, carbon dioxide-free air.

With all the clips closed save Q and R, the air valve was opened and the flasks D and E disconnected, the ends of the syphon tubes being placed in beakers of water through which a fairly rapid stream of air was bubbled. In the meantime, exactly equivalent quantities of pure silver nitrate and pure baryta, sufficient to form about 25 g. of silver oxide, had been weighed out. The silver nitrate was dissolved in 750 c.c. of pure water in the Jena flask, and the solution was boiled out and allowed to cool in an atmosphere free from carbon dioxide. The baryta was dissolved in 750 c.c. of pure water in the silver flask, the whole being heated to effect solution and then allowed to cool in an atmosphere free from carbon dioxide. The baryta contained a small amount of carbonate for which allowance was made when weighing the substance. When both solutions were cold, their respective syphon tubes were washed down with pure water and the flasks replaced in position, a stream of pure air being passed down the syphon tubes during the operation.

About 500 c.c. of pure water were syphoned over into the precipitation vessel. With all screw clips closed, except O, P, R, S, and T, the air valve was opened so that the silver nitrate and baryta solutions were forced over into the precipitation vessel. The clips O and P and the air valve were so adjusted that the solutions entered the precipitation vessel at a slow and, as nearly as could be judged, an equal rate. It was found after a little preliminary practice with

this apparatus that this could be done fairly accurately when syphon tubes of the same diameter were employed. This procedure was devised to minimise any risk of occlusion. The precipitated oxide was allowed to settle for about 6 hours and the supernatant liquid syphoned off by way of N. The precipitation vessel was then filled with wash-water. The apparatus was sufficiently flexible to permit a slight rocking motion being given to the precipitation vessel. By this means a swirling motion was imparted to the wash-water. This brought about mixing but, owing to the heavy nature of the precipitate, was not as efficient as could be desired. After standing for ½ hour in contact with the precipitate and being agitated at intervals, the wash-water was withdrawn *via* the syphon tube. The silver oxide was allowed to drain by raising the plunger very slightly so that the last traces of wash-water dripped through into the funnel. Washing was repeated several times with large quantities of water so that the walls of the precipitation vessel were completely washed down each time. The amount of water was then reduced to one, a half, and finally, a quarter of a litre of water at each washing. The quarter-litre washings were continued until 20 c.c. of the wash-liquor, after standing in contact with the precipitate for ½ hour, gave no turbidity with dilute sulphuric acid on standing in the nephelometer tube for 4 hours. The precipitate was then washed on to the filter and washing continued (the funnel being filled and allowed to drain completely each time) until 200 c.c. of the wash-liquor, acidified with dilute hydrochloric acid and filtered to remove the silver, on evaporation to 20 c.c. showed no precipitate after standing over-night in the nephelometer tube with dilute sulphuric acid. The precipitated silver oxide was allowed to drain while a current of pure air was passed through the apparatus to remove as much water as possible. The filter was then removed from the funnel and quickly transferred to a desiccator containing fused potash. After 3 to 4 weeks the oxide was sufficiently dry to permit of its being roughly powdered. Drying was continued for a further period of 3 weeks over fresh potash, when the oxide was ready for analysis.

The purity of the sample was tested as follows : A small quantity of the oxide was suspended in water and a few drops of dilute hydrochloric acid were added. The production of a white chloride showed that no reduction of the oxide had taken place during drying. The oxide was tested for barium by extracting 2 g. with dilute hydrochloric acid, filtering, and adding to the hot filtrate a few drops of dilute sulphuric acid. After standing over-night, the liquid was examined in the nephelometer. The absence of any turbidity showed the oxide to be free from barium.

The silver nitrate used in the preparation of the pure silver oxide was from four sources:

A. The silver resulting from the A series of preliminary experiments.

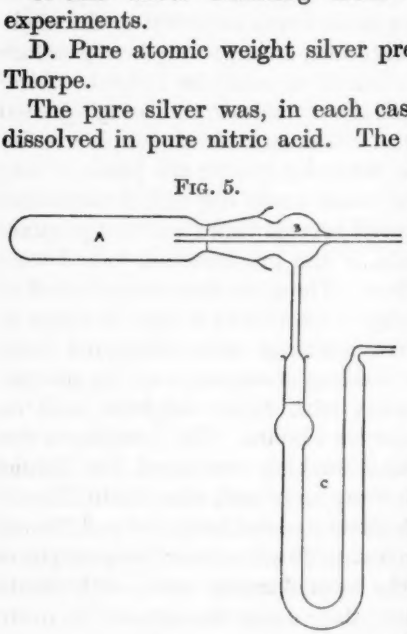
B. The silver resulting from the B series of preliminary experiments.

C. The silver resulting from the C series of preliminary experiments.

D. Pure atomic weight silver prepared by the late Sir Edward Thorpe.

The pure silver was, in each case, after a preliminary etching, dissolved in pure nitric acid. The solution was filtered through a Munroe-Gooch crucible and recrystallised in the manner previously described. Each sample was between 50 and 60 g. in weight.

FIG. 5.



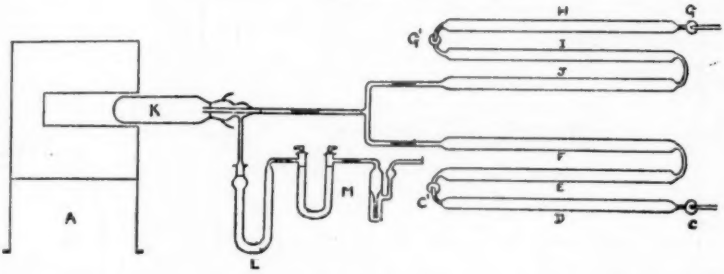
3. *Determination of the Ratio Silver : Oxygen in Silver Oxide.*

Preliminary investigation had shown that it is impossible to remove all the water from precipitated silver oxide by drying at the ordinary temperature. In determining the ratio of silver to oxygen it is therefore necessary to make a correction for the amount of moisture left in the oxide. The apparatus used is shown in Fig. 5. It consists of a thin-walled, transparent silica tube, A, weighing about 50 g. The neck of this tube has been strengthened by thickening the silica and it is ground to fit a glass stopper and a Jena glass adapter, B. The adapter carries a side-arm which connects, through a ground glass joint, with the U-tube, C. The left limb of the U-tube is half filled with fused potash, the bend packed with purified asbestos, and the right limb filled with purified phosphorus pentoxide. Besides the adapter side-tube, the left limb of the U-tube is ground to fit a glass stopper, and a ground glass cap fits the narrowed end of the right limb. As it is impossible to use any lubricant on these ground joints, they were hand-polished until optical contact was made. Under these conditions, the unavoidable small leak was reduced to negligible proportions. Owing to the

greater coefficient of expansion of glass, the silica–glass joint between the silica tube and the adapter becomes gas-tight as soon as heating is commenced.

The method of carrying out a determination of the above ratio is briefly as follows. The silver oxide is weighed in the silica tube and decomposed in a current of pure dry air at 350—400°. The water and any small amount of carbon dioxide in the oxide are retained by the potash and phosphorus pentoxide in the U-tube. The loss in weight of the silica tube and contents (oxygen) may thus be corrected by subtracting the gain in weight of the U-tube. The weight of the residual silver is determined by first displacing the air in the tube by pure hydrogen and then melting the amorphous silver in the atmosphere of hydrogen, cooling, replacing the hydrogen by air and finally weighing.

FIG. 6.



The apparatus is shown in Fig. 6. A (shown in detail in Fig. 7) is the electric furnace used for heating the silica tube. The thin-walled silica tube is wound with seven turns of thin platinum foil about $\frac{1}{8}$ inch in width. This is lagged with heavy magnesia and a thick-walled silica tube. Ten turns of nichrome wire are wound round the thick-walled silica tube and connected in series with the platinum ribbon. The whole is placed in an asbestos box and well lagged with woolly asbestos. The furnace could be safely run at 1200°; it then consumed about 700 watts.

At B is an electrolytic cell (shown in detail in Fig. 8) for the preparation of pure hydrogen. It consists of three glass U-tubes connected in parallel. The electrolyte is a solution of pure barium hydroxide and the electrodes are of platinum foil.

The current of air in which the oxide is decomposed is purified by passing through the bubbler C (containing syrupy phosphoric acid), over copper oxide heated electrically to dull redness in the hard glass tube D, through another phosphoric acid bubbler, C′, and finally through the drying tubes E and F, E containing fused potash and F pure phosphorus pentoxide. The source of air is a

cylinder of compressed air and the flow is regulated by means of an "Endurance" valve. A similar series of purifying tubes is used for the hydrogen. G and G′ are phosphoric acid bubblers. H is a hard glass tube containing copper gauze heated electrically to dull redness. This removes the small amount of oxygen which is carried over with the hydrogen from the baryta cell. I and J are potash and phosphorus pentoxide drying tubes respectively. K is the silica tube and L the U-tube. The ground joints between the adapter and the silica tube and between the adapter and the U-tube are heated electrically to 100° to prevent moisture condensing

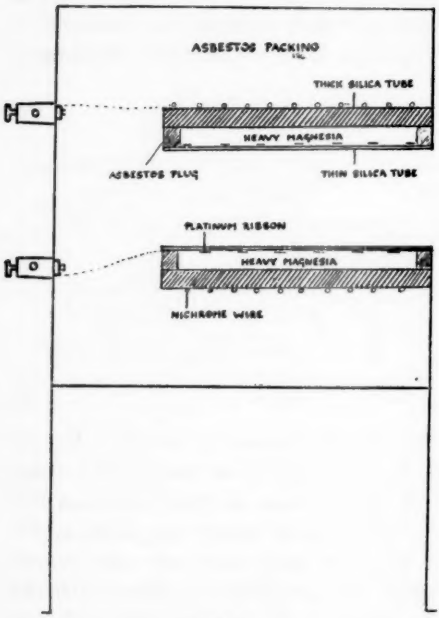


FIG. 7.

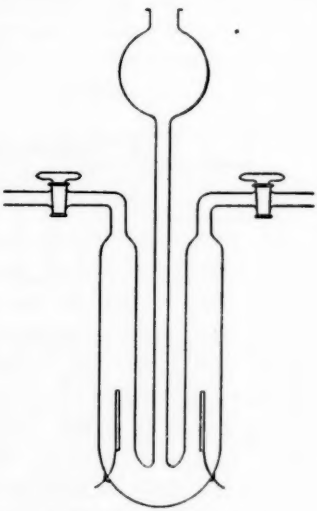


FIG. 8.

anywhere but in the U-tube. M is a guard arrangement, consisting of a pentoxide tube and a phosphoric acid bubbler.

All weighings were carried out on a long beam (No. 5) Oertling balance, kept specially for atomic weight work and previously used in the determination of the atomic weights of tellurium and mercury. The sensitivity of the balance increased slightly with load and was in the neighbourhood of 250 (*i.e.*, a change of load of 0·1 mg. shifted the zero 2·5 divisions of the pointer scale). To cut down any vibration to a minimum the balance-case feet were supported on pads of filter-papers. The weights used were of brass (platinum-plated), the fractions being pure platinum. They were carefully

calibrated, by the method due to Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144), both before and after the determinations. No appreciable change had taken place. All weighings were made against a counterpoise, and the weights corrected to vacuum by the formula: Buoyancy correction $= M\sigma(1/\Delta - 1/\rho)$, where M = mass on balance pan; σ = density of air; Δ = density of substance weighed; and ρ = density of weights employed. The following densities were used: Brass 8·26, platinum 21·5, silver 10·5. That of desiccated silver oxide was measured and found to be 7·10.

Before commencing the determinations a series of blank experiments was performed. These were carried out in an exactly similar manner to the determinations proper and it was found that there was a constant increase in weight of the U-tube after each blank experiment. The mean gain in weight in twelve experiments was 0·24 mg., no single experiment differing from the mean by more than 0·05 mg.

The actual determinations were carried out as follows: The silica tube was heated in the electric furnace to 1100°, the air having been previously displaced by hydrogen. After the tube had cooled, the hydrogen was displaced by air, the adapter removed, and the tube heated to 400° while a current of air was passed through it. The tube was placed while still hot in a desiccator over phosphorus pentoxide and again allowed to cool. It is necessary to remove the adapter before heating for the second time because the silica-glass joint is quite tight at temperatures above normal owing to the greater expansion of the glass. After remaining in the desiccator for ½ hour, the silica tube was removed, stoppered, and placed in the balance case along with another silica tube which had been similarly treated (the counterpoise). The atmosphere in the balance case was kept dry by means of phosphorus pentoxide and potash. After remaining in the balance case for ½ hour, the stoppers were eased, thus adjusting the pressure in each tube to atmospheric. The tubes were then suspended from the arms of the balance and carefully weighed after another ½ hour. Before being placed in the balance-case the silica tubes were lightly dusted with a piece of silk. It was found that only by keeping strictly to the above procedure could the silica tube be kept constant in weight. Any variation in the length of time in the desiccator, heat treatment before weighing, etc., altered the weight in some cases by as much as 0·25 mg.

After being weighed the tube and counterpoise were again heated to 400° and allowed to cool for ½ hour in the desiccator. Before stoppering the silica tube, about 20 g. of pure silver oxide were quickly introduced through a wide-stemmed funnel. The silica tube con-

taining the oxide was now weighed with precautions similar to those employed in weighing the empty tube.

The absorption U-tube, which along with its counterpoise had been placed in the balance-case, was now suspended from the balance arm after the stopper had been eased momentarily in order to adjust the pressure. After ½ hour the U-tube was weighed.

The silica tube and the absorption U-tube were then quickly connected to the hard glass adapter, the heating coils placed in position, and a slow current of air was turned on. The electric furnace was moved carefully over the silica tube, care being taken that the furnace walls did not touch it, and the current was switched on. The rate of evolution of oxygen was controlled by means of a variable resistance and also by sliding the furnace backwards and forwards; it was not allowed to exceed four bubbles per second.

The silver oxide, which was originally decidedly brown, gradually became darker until it was black. As the temperature increased, white specks of metallic silver appeared at the far end of the tube and these grew, as the decomposition progressed, until all the oxide had been converted into white, amorphous silver. This was accompanied by considerable shrinkage, the residual amorphous silver occupying about one-quarter of the original volume of the oxide and still retaining the shape of the silica tube. When decomposition was complete (in about 3 hours) the apparatus was disconnected and the absorption U-tube re-weighed, with all the previous precautions. The gain in weight was noted and, after correction, was subtracted from the weight of silver oxide, thus giving the weight of pure oxide.

The apparatus was then reassembled and the air displaced by pure hydrogen from the baryta cell. In the meantime the electric furnace was switched on and, by the time the air had been displaced, it had acquired the temperature necessary to melt the silver. The furnace was moved up carefully over the silica tube. It was necessary to protect the ground joint between the silica tube and the glass adapter because if this became too hot a fracture resulted. The protection was effected by a piece of asbestos board and by fanning the joint. In about 20 minutes the silver had melted to a bead. The heating was discontinued and the tube allowed to cool slowly. Too rapid cooling cracked the tube owing to the greater contraction of the silver bead, which adhered to the fused quartz surface. When the apparatus was cool the hydrogen was displaced by air. The adapter was then disconnected and the tube heated to 400° in a current of pure air and, while still hot, placed in the desiccator to cool. It was weighed under similar conditions to those employed in the initial weighing.

The silver bead in some cases was found to be coated with a very

thin film of dross. This proved to be silica. It was shown, however, that the weight of this silica, which was always of the order of a fraction of a milligram, was equal to the loss in weight of the silica tube. Apparently the molten silver, or the hot silver oxide, attacks the tube somewhat, and the silica is deposited on the surface of the bead as it cools.

From the loss in weight of the silver oxide and the weight of the residual silver, the value of the ratio silver to oxygen can easily be calculated.

The following are the results of the experiments :

Experiment.

Weights (g.).	1 A.	1 B.	2 B.	1 C.	2 C.	2 D.
$Ag_2O + H_2O$	20·20674	19·43588	21·82606	20·03207	19·47189	21·31387
H_2O	0·06607	0·04469	0·06330	0·07361	0·05963	0·05989
Ag_2O	20·14067	19·39119	21·76276	19·95846	19·41226	21·25398
Ag_2O (vac.) ...	20·14133	19·39186	21·76351	19·95910	19·41287	21·25468
Ag	18·75106	18·05341	20·26123	18·58147	18·07284	19·78749
Ag (vac.)	18·75067	18·05298	20·26076	18·58107	18·07242	19·78708
Oxygen	1·39066	1·33888	1·50275	1·37803	1·34045	1·46760
Ratio O : Ag = 8 :	107·866	107·869	107·861	107·870	107·859	107·861

Mean ..... 107·864 ± 0·0013

4. *The Action of Light on Silver Oxide.*

The desiccated silver oxide, prepared as previously described, has a decided brown colour, quite free from the purplish-black colour usually associated with the compound. A sample of the oxide exposed to daylight in a closed glass vessel over a period of several weeks showed no alteration in colour. The oxide used in the atomic weight determination was prepared in a darkened room and only exposed to red light in order to be quite sure that no decomposition took place, but it is doubtful whether this precaution was necessary. A sample of the oxide exposed to daylight in an open vessel darkened slowly and in the course of a day or two became almost black. This darkening was probably due to the reduction of the oxide by the organic matter in the atmosphere.

Some of the preliminary work on this subject was carried out in conjunction with Messrs. E. Skelton, T. T. H. Verschoyle, and R. W. Farnell, to whom the authors express their sincere thanks. We are also indebted to Messrs. Brunner Mond and Co., a grant from whom covered a large part of the expense of this research. One of us (H. L. R.) wishes to place on record his thanks to the Trustees of the Beit Scientific Research Fellowships for election to a Fellowship which enabled him to participate in this investigation.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, June 4th*, 1926.]

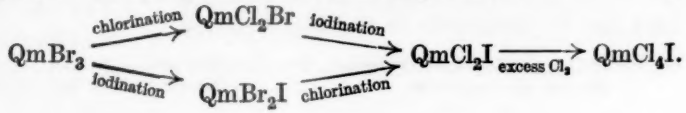
CCCXXXI.—*Quaternary Ammonium Perhalides.*

By THOMAS HAROLD READE.

WHEN quaternary ammonium halides are treated with chlorine, bromine, or iodine, addition compounds are formed containing three halogen atoms. These trihalides are coloured substances which are stable enough to be recrystallised from alcohol or acetic acid. To this class belong, not only tri-iodides and tribromides—one trichloride only is known—but also "mixed" trihalides (*e.g.*, dibromoiodides) which have been investigated by McCombie and Reade (J., 1923, **123**, 143), Reade (J., 1924, **125**, 148), and by Reade and Sim (J., 1924, **125**, 157).

The trihalides are often referred to as "molecular compounds," but the term is misleading, for, although a dichloroiodide is obtained by chlorinating an iodide, the substance decomposes into the chloride and iodine monochloride, but not into the two components from which it was formed.

The facts that the absorption spectra of quaternary ammonium trihalides and of the corresponding metallic trihalides are almost identical, and that sulphates and nitrates do not form stable addition-products with the halogens whereas chlorides, bromides, and iodides do so, are most simply interpreted as signifying the existence of complex trihalogen ions in these compounds. The chemical properties of the three halogen atoms in a trihalide are not, however, identical. Means of splitting off halogen atoms from trihalides were described by McCombie and Reade (*loc. cit.*), and constitutional formulæ based on this process were tentatively put forward for trihalides. For example, a dichloroiodide was regarded as an addition compound of the chloride and iodine monochloride because the quaternary ammonium chloride exclusively was precipitated when the trihalide was dissolved in warm acetone. Since, however, it is now known that the relative solubilities in acetone of the quaternary ammonium halides are far from equal, and since the least soluble will tend to accumulate if the trihalide can decompose in more than one way, the constitutional deductions previously put forward are open to question. The evidence afforded by the results of submitting these trihalides to the further action of the halogens, which is set forth in the table (p. 2530), shows that electrical charge also must be taken into account. The reasoning employed will be clear from the following scheme.



When a tribromide Qm*Br_3 is chlorinated it gives a dichlorobromide, one bromine atom escaping replacement; when it is iodinated, however, only one bromine atom is replaced, a dibromoiodide resulting. The atom which is replaced in the latter process must be the same as that which is unaffected during the chlorination, because it can be displaced by iodine from the dichlorobromide, giving the dichloroiodide. This argument can be submitted to a further check by determining whether the two bromine atoms which are displaced by chlorine from the tribromide are the same two as those which escape displacement by iodine; if so, then the two bromine atoms in the dibromoiodide should be displaceable by chlorine, but the iodine should remain. This is confirmed by experiment, for the product is the dichloroiodide $QmCl_2I$, a large excess of chlorine giving the tetrachloroiodide $QmCl_4I$.

The conclusion is irresistible that in a tribromide two bromine atoms behave alike and are replaceable only by the lighter halogen, whereas the third bromine atom is replaceable only by the heavier halogen, iodine. The former behaviour is characteristic of negatively charged bromine, as in the ordinary bromide ion, the latter of the halogen in a bromate. But since the tribromide ion carries a single negative charge and yet contains two negatively charged atoms, the remaining bromine atom must be electropositive. The tribromide would then be represented as $\overset{+}{Qm} \ldots \overset{-}{Br}\overset{+}{Br}\overset{-}{Br}$ so far as charge alone is concerned.

This tendency amongst trihalides for one atom to function electropositively whilst the remaining two atoms are negatively charged appears to be quite general, and can be traced throughout all the reactions shown in the table. Although it is more difficult to detect in the lower half of the table, where the formation of more than one trihalide frequently occurs, the principle is never actually violated. To be more precise, where a single trihalide is formed, there are 100% of agreements; where two trihalides are simultaneously produced, one always agrees whilst one disagrees, thus affording neither proof nor disproof. Neglecting the latter, the probability of a fortuitous agreement with this generalisation is so extremely small—about 1 in 10^{15}—as to be negligible.

One further question arises: If the formula of a trihalide is known, is it possible to predict which halogen atom will behave electropositively and which two negatively? Reference to the table shows that the electropositive atom is always the heaviest halogen which the trihalide complex contains.

It is of interest that crystals of metallic trihalides appear to

* Qm denotes the phenyltrimethylammonium radical.

have the heaviest halogen atom between the other two halogen atoms, the three atoms being in line along the diagonal of the cell the corners of which are occupied by the metal (Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100; Clark, *Proc. Nat. Acad. Sci.*, 1922, **8**, 90). The central atom spatially is that of highest atomic weight; it is also the atom the chemical properties of which indicate that it is positively charged. This is probably the reason why dichlorobromides are less stable than dichloroiodides, whilst trichlorides are so unstable that only one has so far been isolated, for the tendency for the halogens to function electropositively admittedly decreases in the order iodine, bromine, chlorine.

The view to which these considerations lead is that the chemical reactions of quaternary ammonium trihalides are more directly dependent upon the electrical charges carried by the three halogen atoms than upon the arrangement of these atoms in space. It now becomes clear why the common classification of quaternary ammonium trihalides as "molecular compounds" is so much out of harmony with many of their chemical reactions; for to regard a dichloroiodide as a molecular compound of chlorine and a quaternary ammonium iodide implies that the iodine atom still retains its negative charge, whereas actually it functions electropositively.

The following table contains a complete summary of experiments in which a trihalide has been chlorinated, brominated, or iodinated in glacial acetic acid, and is largely taken from previously published papers (see McCombie and Reade, *loc. cit.*; Reade, *loc. cit.*). In accordance with the ideas developed in this communication, the heaviest halogen in each trihalide is written centrally.

	Qm = Phenyltrimethylammonium.			Qm = *p*-Bromophenyltrimethylammonium.		
	Product of halogenation by			Product of halogenation by		
Trihalide.	chlorine.	bromine.	iodine.	chlorine.	bromine.	iodine.
Qm–ClICl	–ClICl –ClICl$_3$	–ClICl	–ClICl	–ClICl$_3$	–ClICl –BrICl	–ClICl*
Qm–BrICl	–ClICl$_3$	–BrICl	–BrICl	–ClICl$_3$	–BrICl –BrIBr	–BrICl –BrII
Qm–BrIBr	–ClICl$_3$	–BrIBr	–BrIBr –BrII	–ClICl$_3$	–BrIBr	–BrIBr –BrII
Qm–ClBrCl	–ClBrCl	–ClBrCl	–ClICl	–ClBrCl	–ClBrCl	–ClICl –BrICl
Qm–BrBrBr	–ClBrCl	–BrBrBr –Br$_5$	–BrIBr	–ClBrCl	–BrBrBr	–BrIBr
Qm–BrII	–ClICl$_3$	–BrIBr	–BrII	–ClICl$_3$	–BrIBr	–BrII –I$_3$
Qm–III	–ClICl$_3$	–BrIBr	–I$_5$	–ClICl$_3$	–BrIBr	–III –I$_5$

* Also products containing iodine.

Experimental.

The solubilities in acetone of *p*-bromophenyltrimethylammonium chloride, bromide, and iodide were determined by shaking an excess of each salt with warm acetone, and then leaving it with occasional shaking in a thermostat at 15° for 24 hours. 25 C.c. of the filtered saturated solution were boiled with aqueous silver nitrate and the silver halides were weighed: 25 c.c. gave 0·0356 g. AgCl, 0·0079 g. AgBr, and 0·0101 g. AgI, respectively; whence 100 c.c. of acetone dissolved 0·000992 g.-mol. $C_6H_4Br{\cdot}NMe_3Cl$, 0·000168 g.-mol. $C_6H_4Br{\cdot}NMe_3Br$, and 0·000172 g.-mol. $C_6H_4Br{\cdot}NMe_3I$.

Iodination of p-*Bromophenyltrimethylammonium Dichlorobromide.*—0·94 G. of iodine in 40 c.c. of acetic acid was shaken with 1·36 g. of *p*-bromophenyltrimethylammonium dichlorobromide in 60 c.c. of acetic acid and set aside for 24 hours in a cool place. The crystals which separated were fractionally crystallised from acetic acid. The more soluble portion was identified as *p*-bromophenyltrimethylammonium chlorobromoiodide, m. p. 178°, by comparison with an authentic specimen. The less soluble portion, m. p. 176°, was identified as the dichloroiodide, by conversion by acetone into *p*-bromophenyltrimethylammonium chloride, the double salt of which with mercuric chloride was analysed (Found: Cl, 19·3. $C_9H_{13}NClBr,HgCl_2$ requires Cl, 20·4%). The original mother-liquor was proved to contain iodine monochloride and iodine monobromide by adding it to aqueous potassium iodide solution, removal of iodine and acetic acid by distillation, addition of sodium nitrite, extraction five times with chloroform, and precipitation of the halides with silver nitrate (Found: Br, 0·0363 g.; Cl, 0·0110 g.). The complete reaction is therefore $2I_2 + 2C_6H_4Br{\cdot}NMe_3Cl_2Br \longrightarrow C_6H_4Br{\cdot}NMe_3ClBrI + C_6H_4Br{\cdot}NMe_3Cl_2I + ICl + IBr$.

University of Aberdeen. [*Received, March 12th*, 1926.]

CCCXXXII.—*Some Thiazole Derivatives. Part I.*

By Herbert William Stephen and Forsyth James Wilson.

It was shown by Wilson and Burns (J., 1922, **121**, 870; 1923, **123**, 799) that the sodium derivative of acetonethiosemicarbazone reacted with esters of α-halogeno-acids to produce thiazole derivatives. This work has now been extended.

Acetone-δ-phenylthiosemicarbazone was treated in alcoholic solution with esters of α-halogeno-acids in presence of sodium ethoxide; the reaction proceeded smoothly as in previous cases,

giving in excellent yield the 2-*iso*propylidenehydrazone of a 2 : 4-diketotetrahydrothiazole.

$$CMe_2{:}N{\cdot}N{:}C(SNa){\cdot}NHPh + CHRBr{\cdot}CO_2Et =$$
$$NaBr + EtOH + CMe_2{:}N{\cdot}N{:}C\begin{cases}NPh{\cdot}CO\\ S\text{——}CHR\end{cases} \quad (I.)$$

The esters employed were ethyl chloroacetate, ethyl α-bromo-*n*-butyrate, and ethyl phenylbromoacetate. By analogy with previous work, it was expected that dilute or concentrated acids would effect hydrolysis as shown by (*a*) or (*b*) respectively :

$$NH_2{\cdot}N{:}C\begin{cases}NPh{\cdot}CO\\ S\text{——}CHR\end{cases},HCl \quad (II.) \xleftarrow{(a)} (I.) \xrightarrow{(b)} OC\begin{cases}NPh{\cdot}CO\\ S\text{——}CHR\end{cases} \quad (III.)$$
$$+Me_2CO \qquad\qquad +Me_2CO + N_2H_4,2HCl$$

In previous cases these two stages were sharply distinguished, but in the present instances the hydrolysis could not be arrested at the first stage; it was therefore carried to completion with concentrated acid, but the yields of 2 : 4-diketo-3-phenyl-5-R-tetrahydrothiazole (III) were small, considerable decomposition taking place.

In the expectation of obtaining a compound with a thiazole ring fused on to another ring structure, experiments were carried out with ethylenethiocarbamide. This substance gave a sodium derivative with sodium ethoxide, but it was not necessary to isolate it, for it reacted *in situ* with ethyl (or methyl) chloroacetate in hot alcoholic solution, giving in good yield *ethyl* (or *methyl*) 4 : 5-*dihydroiminazole*-2-*thioglycollate* (IV).

$$\begin{matrix}CH_2{\cdot}NH\\ CH_2\text{—}N\end{matrix}\!\!>\!C{\cdot}SNa + CH_2Cl{\cdot}CO_2Et = NaCl + \begin{matrix}CH_2{\cdot}NH\\ CH_2\text{—}N\end{matrix}\!\!>\!C{\cdot}S{\cdot}CH_2{\cdot}CO_2Et. \quad (IV.)$$

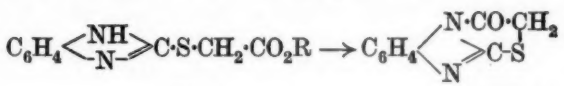
Efforts to effect ring closure with this compound so as to produce 4 : 5-*dihydroiminazole*-2-*thioglycollo*-1-*lactam* (V), were unsuccessful. It was found, however, that this substance could be formed in small yield by heating ethylenethiocarbamide with either ethyl or *n*-butyl chloroacetate in pyridine solution :

$$\begin{matrix}CH_2{\cdot}NH\\ CH_2\text{—}N\end{matrix}\!\!>\!C{\cdot}SH + CH_2Cl{\cdot}CO_2R + C_5H_5N =$$
$$ROH + C_5H_5N,HCl + \begin{matrix}CH_2{\cdot}N{\cdot}CO{\cdot}CH_2\\ CH_2{\cdot}N\end{matrix}\!\!>\!C{\cdot}S \quad (V.)$$

Experiments in which *o*-phenylenethiocarbamide was substituted for ethylenethiocarbamide gave much more definite results. The *sodium* derivative of this thiocarbamide was isolated in a pure state, but, as in previous cases, an alcoholic solution of the thiocarbamide to which 1 mol. of sodium ethoxide had been added was used.

This solution when heated for a short time with ethyl chloroacetate gave *ethyl benziminazole-2-thioglycollate* (VI); the *methyl* ester was prepared in the same way.

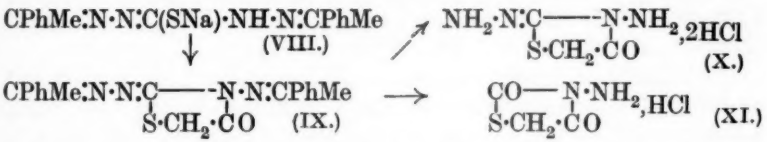
Ring-closure with these esters was effected by heating in benzene solution with sodium powder, the same substance, *benziminazole-2-thioglycollo-1-lactam* (VII), being produced from either ester.



(VI.) (VII.)

The yield was, however, only 25% and could not be improved.

The production of thiazoles from thiocarbohydrazones was next investigated. We had intended to make a general study of aldehydic and ketonic thiocarbohydrazones, but while this work was in progress a paper by Guha and Dey (*J. Indian Chem. Soc.*, 1925, 2, 225) appeared, in which a number of thiocarbohydrazones were described. We have therefore modified our programme and have dealt with the application of these compounds in thiazole formation. A few thiocarbohydrazones which we had prepared are described in the experimental part. Diacetophenonethiocarbohydrazone, the *sodium* derivative (VIII) of which we prepared, was found to be the most suitable for use. It reacted in alcoholic solution with ethyl chloroacetate in presence of sodium ethoxide in the usual manner, giving 3-*phenylmethylmethyleneamino*-2 : 4-*diketotetrahydrothiazole*-2-*phenylmethylmethylenehydrazone* (IX) in excellent yield. This compound on hydrolysis with dilute hydrochloric acid gave



(VIII.) (X.) (IX.) (XI.)

acetophenone and 3-*amino*-2 : 4-*diketotetrahydrothiazole*-2-*hydrazone dihydrochloride* (X), an extremely deliquescent solid giving a *dibenzylidene* derivative. On the other hand, hydrolysis with concentrated hydrochloric acid yielded acetophenone, hydrazine hydrochloride, and 3-*amino*-2 : 4-*diketotetrahydrothiazole hydrochloride* (XI), also a very deliquescent solid which gave a *benzylidene* derivative. Both hydrochlorides were obtained in good yield, but attempts to prepare the pure bases from them were unsuccessful.

It is believed that the dicyclic systems described are new. This work will be continued.

Experimental.

Experiments with Acetone-δ-phenylthiosemicarbazone.

This substance was prepared by adding a slight excess of acetone to a boiling saturated alcoholic solution of the thiosemicarbazide and continuing the boiling for 15 minutes. It separated on cooling and was recrystallised from alcohol as glistening plates, m. p. 130°, soluble in alcohol, ether, and benzene; yield 90% (Found : N, 20·4, 20·3. $C_{10}H_{13}N_3S$ requires N, 20·3%). The sodium derivative could not be obtained in a pure state.

With Ethyl Chloroacetate.—The necessary quantity of sodium ethoxide in alcohol was added to a boiling saturated alcoholic solution of the δ-phenylthiosemicarbazone; after heating this solution for 5 minutes, the ester (1 mol.) was added. A vigorous reaction occurred with separation of a flocculent, yellow solid. After heating for ½ hour and cooling, the solid was collected, washed with warm water, and recrystallised from alcohol (charcoal). Fine, almost colourless needles of 2 : 4-*diketo*-3-*phenyltetrahydrothiazole*-2-iso*propylidenehydrazone* (I, R = H), m. p. 200°, were deposited; yield 70% (Found : N, 17·0, 16·9. $C_{12}H_{13}ON_3S$ requires N, 17·0%). The substance was hydrolysed by boiling for 3 hours with concentrated hydrochloric acid; the solution was then evaporated to dryness and the residue, after standing in a vacuum over soda-lime and concentrated sulphuric acid and then being washed with cold water to remove hydrazine hydrochloride, was recrystallised from water. The needles, m. p. 143°, were identical with 2 : 4-diketo-3-phenyltetrahydrothiazole (III, R = H), described by Evers (*Ber.*, 1888, **21**, 975) and by Lange (*ibid.*, 1879, **12**, 597); yield, small (Found : N, 7·3. Calc. : N, 7·3%).

With Ethyl α-Bromo-n-butyrate.—The reaction was carried out as before, the sodium bromide which separated in the heat being filtered off and washed with a little absolute alcohol; the filtrate and washings on cooling deposited 2 : 4-*diketo*-3-*phenyl*-5-*ethyltetrahydrothiazole*-2-iso*propylidenehydrazone* (I, R = Et), fine needles from alcohol, m. p. 131°, yield 75% (Found : N, 15·2, 15·3. $C_{14}H_{17}ON_3S$ requires N, 15·3%). Boiling with concentrated hydrochloric acid (3 hours) gave on cooling 2 : 4-*diketo*-3-*phenyl*-5-*ethyltetrahydrothiazole* (III, R = Et), feathery needles from water, m. p. 98°; yield small, extensive decomposition having occurred (Found : N, 6·5. $C_{11}H_{11}O_2NS$ requires N, 6·3%).

With Ethyl Phenylbromoacetate.—The reaction, carried out as in the first case, gave a flocculent precipitate which was collected after ¼ hour's heating, and washed with warm water. Recrystallisation from acetone gave 2 : 4-*diketo*-3 : 5-*diphenyltetrahydrothiazole*-

2-iso*propylidenehydrazone* (I, R = Ph), hair-like needles, m. p. 189°, yield 75%, insoluble in water and ether, sparingly soluble in alcohol (Found: N, 13·0, 13·0. $C_{18}H_{17}ON_3S$ requires N, 13·0%). Hydrolysis of this substance with concentrated hydrochloric acid did not lead to a definite result.

Experiments with Ethylenethiocarbamide.

This substance was prepared by Hofmann's method (*Ber.*, 1872, **5**, 242) and melted at 196° (Hofmann gives 194°) (Found: N, 27·5. Calc.: N, 27·5%). The sodium derivative was obtained in an impure state only.

An absolute alcoholic solution of the thiocarbamide was boiled for 10 minutes with sodium ethoxide (1 mol.); ethyl chloroacetate (1 mol.) was then added and the boiling continued for ½ hour. The solution, after being filtered while hot from sodium chloride, deposited on cooling *ethyl* 4 : 5-*dihydroiminazole*-2-*thioglycollate* (IV), needles from absolute alcohol, which began to decompose at about 160°, turning pink, and melted at 190° to a dark red liquid. It was very soluble in water and alcohol, insoluble in ether, light petroleum, and benzene. The best yield was obtained by using the minimum quantity of alcohol, as concentration of the mother-liquors caused decomposition (Found: N, 15·0; S, 17·2. $C_7H_{12}O_2N_2S$ requires N, 15·0; S, 17·0%). The formation of thioglycollic acid (recognised by Andreasch's test) and ethyl alcohol on hydrolysis with sodium hydroxide proved the presence of the group ·S·CH_2·CO_2Et in this compound. The *methyl* ester (needles from absolute alcohol), prepared in the same way from methyl chloroacetate, showed a similar solubility; it began to decompose at about 170° and melted at 190° (Found: N, 16·0; S, 18·6. $C_6H_{10}O_2N_2S$ requires N, 16·1; S, 18·4%); best yield about 80%. Attempts in various ways to effect ring-closure with these esters were unsuccessful.

Ethyl chloroacetate was added to a hot pyridine solution of ethylenethiocarbamide (1 mol.) and the whole was boiled for ½ hour. The dark-coloured solution was evaporated to dryness under reduced pressure and the gummy residue dissolved in hot absolute alcohol. The crystals deposited on cooling gave, on recrystallisation from absolute alcohol, colourless plates of 4 : 5-*dihydroiminazole*-2-*thioglycollo*-1-*lactam* (V), m. p. 159°, yield 10—20% (Found: N, 19·7. $C_5H_6ON_2S$ requires N, 19·7%). It was readily soluble in water and alcohol, but insoluble in other common solvents, and showed Andreasch's test for thioglycollic acid after heating with alkali. The same substance was obtained by substituting *n*-butyl chloroacetate for the ethyl ester in the above method of preparation, the identity being established by a mixed m. p. determination. The

compound, in spite of repeated experiments, was obtained on these two occasions only; further attempts led apparently to complex mixtures.

Experiments with o-*Phenylenethiocarbamide.*

The *sodium* derivative, prepared by mixing a hot absolute alcoholic solution with sodium ethoxide (1 mol.) in alcohol, heating for 10 minutes, and then concentrating, was an almost white powder giving an alkaline reaction (Found: Na, 13·4. $C_7H_5N_2SNa$ requires Na, 13·3%).

An absolute alcoholic solution of the thiocarbamide was boiled with sodium ethoxide (1 mol.); ethyl chloroacetate was then added and the heating continued for ½ hour. After filtration from sodium chloride, the solution did not crystallise even on concentration; addition of a little water, however, caused turbidity and crystals separated on standing, more being deposited on further dilution. This substance, *ethyl benziminazole-2-thioglycollate* (VI), when freshly recrystallised from ether–light petroleum or dilute alcohol, melted at 73°, but in a very few minutes a change occurred and it then melted sharply at 97°, this modification, rhombic prisms, being quite stable; this may be a case of dimorphism, but the change was too rapid for investigation. Yield 85% (Found: N, 11·9; S, 13·7. $C_{11}H_{12}O_2N_2S$ requires N, 11·9; S, 13·6%). The *methyl* ester (yield 80%), prepared in the same way using methyl chloroacetate, showed a similar solubility and the same peculiarity as regards m. p. (metastable form at 72°; stable form, rhombic prisms, at 83°) (Found: N, 12·6; S, 14·4. $C_{10}H_{10}O_2N_2S$ requires N, 12·6; S, 14·4%). Neither ester developed any noticeable blackening on heating with very concentrated sodium hydroxide solution and subsequent addition of a lead salt, whilst *o*-phenylenethiocarbamide itself produced strong blackening under these conditions; this is in conformity with the presence of the group C–S–C in these esters.

Sodium powder (excess) was added to a hot benzene solution of the ethyl ester and the heating was continued for ½ hour under reflux on the water-bath. A deep yellow colour developed and a yellow solid was deposited; the benzene solution after decantation, filtration and evaporation to dryness left a residue which on recrystallisation from alcohol gave *benziminazole-2-thioglycollo-1-lactam* (VII), prismatic needles, m. p. 181°, yield 25% (Found: N, 14·7; S, 17·0; *M*, ebullioscopic in benzene, 187. $C_9H_6ON_2S$ requires N, 14·7; S, 16·8%; *M*, 190). There was a considerable amount of unchanged ester, and by carrying out the reaction on the water-bath the formation of the yellow compound was minimised. The methyl ester gave the same result.

Experiments with Thiocarbohydrazones.

Thiocarbohydrazide was prepared by the method of Stollé and Bowles (*Ber.*, 1908, **41**, 1099).

Diacetonethiocarbohydrazone, $(CMe_2{:}N{\cdot}NH)_2CS$, obtained by heating under reflux thiocarbohydrazide with excess of dry acetone for several hours and concentration of the solution, crystallised from alcohol–light petroleum in prismatic plates, m. p. 192° (decomp.), very soluble in alcohol and acetone; yield 90% (Found: N, 30·3. Calc. for $C_7H_{14}N_4S$: N, 30·1%).

Diacetophenonethiocarbohydrazone, $(CMePh{:}N{\cdot}NH)_2CS$, was deposited with production of a yellow colour by boiling the components (ketone in slight excess) in alcoholic solution for 1 hour. It crystallised from alcohol–chloroform in very pale yellow, fine, prismatic needles, m. p. 199° with darkening in colour from 175° upwards; very soluble in chloroform, soluble in benzene, sparingly soluble in alcohol, ether, and light petroleum, yield 90—95% (Found: N, 18·1; S, 10·3. Calc. for $C_{17}H_{18}N_4S$: N, 18·1; S, 10·3%).

These two substances have been prepared by Guha and Dey (*loc. cit.*) by methods differing in detail from ours. We found that in making the diacetone derivative prolonged boiling was necessary before the correct analytical results could be obtained, the nitrogen values otherwise being high. Guha and Dey give the m. p.'s of the diacetone and diacetophenone derivatives as 195° and 185°, respectively.

Bis-dibenzyl ketone thiocarbohydrazone, $[C(CH_2Ph)_2{:}N{\cdot}NH]_2CS$, was prepared by heating the components (ketone in slight excess) in alcoholic solution until a clear yellow solution resulted. The solid which separated on cooling crystallised from alcohol in fine, colourless needles, m. p. 143°, soluble in the usual solvents except light petroleum, yield 90% (Found: N, 11·4; S, 6·4. $C_{31}H_{30}N_4S$ requires N, 11·4; S, 6·5%).

Reactions with Diacetophenonethiocarbohydrazone.—The *sodium* derivative was obtained as a yellow powder by adding sodium ethoxide (1 mol.) to an absolute alcoholic suspension of the thiocarbohydrazone, heating for 10 minutes, and then precipitating the cooled yellow solution with ether. It was washed with ether and dried over sulphuric acid; it gave an alkaline aqueous solution (Found: Na, 6·9. $C_{17}H_{17}N_4SNa$ requires Na, 6·9%).

To a boiling alcoholic solution of the sodium derivative ethyl chloroacetate was added in very slight excess and the boiling continued for ½ hour. Sodium chloride was filtered off in the heat, and on cooling 3-*phenylmethylmethyleneamino*-2 : 4-*diketotetrahydrothiazole*-2-*phenylmethylmethylenehydrazone* (IX) was deposited; colourless needles from alcohol–benzene, m. p. 175°, insoluble in

water and light petroleum, soluble in alcohol, benzene, and chloroform; yield 85% (Found: N, 16·0; S, 9·3. $C_{19}H_{18}ON_4S$ requires N, 16·0; S, 9·1%). This compound was boiled under reflux for about 10 minutes with a slight excess of *N*-hydrochloric acid, the acetophenone was removed by decantation and ether-extraction, and the aqueous solution was evaporated to small bulk under reduced pressure and finally to dryness in a vacuum over sulphuric acid and soda-lime. The residue, *3-amino-2 : 4-diketotetrahydrothiazole-2-hydrazone dihydrochloride* (X), was a crystalline, extremely deliquescent solid which had to be manipulated in a dry atmosphere (Found: S, 14·5. $C_3H_6ON_4S,2HCl$ requires S, 14·6%). The *dibenzylidene* derivative, glistening plates from alcohol, melted at 138° (Found: N, 17·5. $C_{17}H_{14}ON_4S$ requires N, 17·4%).

The hydrolysis of the compound of m. p. 175° was carried a stage further by boiling in an open vessel with concentrated hydrochloric acid for about ½ hour. After removal of the acetophenone by ether, the aqueous solution was evaporated to dryness on the water-bath and finally in a vacuum over sulphuric acid and soda-lime. The residue after washing with dry ether was extracted with a little hot absolute alcohol, hydrazine hydrochloride remaining undissolved; the extract on evaporation in a vacuum over sulphuric acid gave a highly deliquescent solid, which was dried for several days in a vacuum over phosphoric anhydride. It was *3-amino-2 : 4-diketotetrahydrothiazole hydrochloride* (XI) (Found: S, 19·0, 19·1. $C_3H_4O_2N_2S,HCl$ requires S, 19·0%). The *benzylidene* derivative crystallised from alcohol in fine, colourless needles, m. p. 158° (Found: S, 14·6. $C_{10}H_8O_2N_2S$ requires S, 14·5%).

We wish to thank the Department of Scientific and Industrial Research for a maintenance grant to one of use (H. W. S.). Our thanks are also expressed to the Carnegie Trust for the Universities of Scotland for a research grant in aid of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, July 13th*, 1926.]

CCCXXXIII.—*Conductivities of Some Organic Salts of Beryllium.*

By NEVIL V. SIDGWICK and NEIL B. LEWIS.

RECENTLY (this vol., p. 1287) we showed that the molecular conductivity of beryllium oxalate solution was practically constant at concentrations from 0·16 to 0·8*N*, and that the product of conductivity and viscosity actually passed through a minimum at

about 0·1*N*. We have now examined the behaviour of the acetate and malonate.

Beryllium Acetate.—The solution was made by adding the equivalent of barium acetate to a solution of pure beryllium sulphate in conductivity water, and filtering. It was free from barium and sulphate ions. The conductivities and viscosities were measured as described in our previous paper; they are given in Table I. The conductivities are low compared with those of the chloride (*loc. cit.*, p. 1296), being about $\frac{2}{5}$ at 0·01*N*, $\frac{1}{4}$ at 0·13*N*, and $\frac{1}{6}$ at 0·5*N*, which indicates the presence of much non-polar form; but unlike those of the oxalate they decrease regularly with rise of concentration.

Beryllium Malonate.—There seems to be no convenient method for preparing solutions of the malonate or succinate by double decomposition. The reaction of the oxalate with magnesium malonate or succinate cannot be used, since magnesium oxalate, although only slightly soluble in water (0·4 g. per litre at 25°), readily forms supersaturated solutions containing up to 200 times as much salt (Kohlrausch and Mylius, *Ber.*, 1904, **37**, 1223). Precipitated beryllium hydroxide could not be washed sufficiently free from salts to be suitable for making the solutions. Solutions of the malonate were ultimately prepared by dissolving the basic carbonate in the required quantity of acid and filtering. They were slightly turbid and apparently supersaturated, since on standing they slowly deposited a white precipitate of basic salt; but if they were not heated this precipitation was very slow, and with the strongest solution used the conductivity only fell 3% in 20 hours; with the more dilute solutions, the fall was much less, so that no serious error was to be expected from this cause in an experiment lasting 4 hours.

With the succinate the precipitation is considerably greater: the deposit was shown to be basic, containing after drying at 100° 9·70% Be [$BeC_4H_4O_4$ requires Be, 7·21; $BeC_4H_4O_4,Be(OH)_2$ requires Be, 10·74%]. The succinate was therefore not examined further. The results for the malonate are given in Table II.

In the tables, the four columns in each case show the equivalent normality (N), the relative viscosity (η), the equivalent conductivity (λ), and the product ($\lambda\eta$) for beryllium acetate and malonate solutions at 25°.

Discussion of Results.

It will be seen that whilst the acetate behaves normally, the molecular conductivity falling continuously as the concentration increases, the malonate resembles the oxalate in that its conductivity is constant over a large range. The only parallel case known is

TABLE I.

Beryllium acetate.

N.	η.	λ.	$\lambda\eta$.
0·00433	(1·001)	50·92	50·9
0·01390	(1·004)	41·62	41·8
0·02187	(1·006)	37·60	37·8
0·03273	(1·009)	34·17	34·5
0·05310	(1·015)	29·82	30·2
0·07896	(1·022)	26·71	27·3
0·1314	(1·037)	22·41	23·3
0·2173	(1·061)	18·38	19·5
0·2610	(1·073)	16·98	18·2
0·3155	1·088	15·45	16·8
0·6410	1·181	11·16	13·2

TABLE II.

Beryllium malonate.

N.	η.	λ.	$\lambda\eta$.
0·00309	(1·000)	8·31	8·31
0·00651	(1·001)	7·85	7·86
0·01421	(1·003)	7·56	7·58
0·02696	(1·005)	7·54	7·58
0·04155	(1·008)	7·51	7·57
0·06546	(1·013)	7·49	7·58
0·09225	(1·018)	7·47	7·60
0·1212	(1·024)	7·46	7·64
0·1584	(1·031)	7·46	7·69
0·2108	(1·041)	7·45	7·75
0·2981	(1·058)	7·39	7·81
0·4563	(1·089)	7·30	7·94
0·6244	1·123	7·19	8·07
1·245	1·274	6·60	8·41

that of the alkaline salts of the highest fatty acids (McBain and co-workers, *Z. physikal. Chem.*, 1911, **76**, 179; J., 1911, **99**, 191; 1912, **101**, 2042; 1914, **105**, 967), but McBain's explanation of the phenomenon by micelle formation cannot apply to these beryllium salt solutions, of which the viscosities are quite small (less than those of the beryllium salts of strong acids); moreover, the conductivities, unlike those of the soap solutions, are abnormally low.

The low conductivity of the malonate is no doubt due (like that of the oxalate) to the presence of a non-polar cyclic form $Be<^{O-CO}_{O-CO}>CH_2$. The abnormal constancy of the conductivity on dilution can be explained by assuming that the Ox″ ion (Ox″ = C_2O_4 or $CH_2{\cdot}C_2O_4$) combines with undissociated BeOx to form a stable complex ion $[BeOx_2]''$. Evidence of the existence of these complexes (containing the stable 4-covalent beryllium) is given by the ready formation of double oxalates, $R_2Be(C_2O_4)_2,nH_2O$ (Rosenheim and Woge, *Z. anorg. Chem.*, 1897, **15**, 283), and double malonates, $R_2Be(CH_2{\cdot}C_2O_4)_2,nH_2O$ (Meyer and Mantel, *ibid.*, 1922, **123**, 43), with ammonium and the alkali metals. The main reaction of ionisation in all but very dilute solutions will then be

$$2BeOx \rightleftharpoons Be^{\cdot\cdot} + [BeOx_2]''.$$

Since in this reaction the number of molecules on each side is the same, the equilibrium (and hence the molecular conductivity) will be independent of the dilution. In very dilute solution, the further dissociation of the complex into $Be^{\cdot\cdot}$ + Ox″ will be increasingly important, and the molecular conductivity will rise, as it is found to do. If this hypothesis is sound, the van 't Hoff factor i should be very little greater than 1: the values found for the oxalate (Sidgwick and Lewis, *loc. cit.*) are 1·13 at 0·2N, and 1·05 at 0·7N. The

minimum conductivity is reached by the oxalate at about 0·1*N*, and by the malonate at about 0·03*N*, indicating that the latter gives the more stable complex; the minimum for the malonate is also about 25% less than for the oxalate.

It was pointed out in our previous paper that the presence of 3 mols. of water (and not 4) in the oxalate can be explained by supposing that in the non-polar beryllium oxalate 2 mols. are attached to the beryllium (giving it a covalency of 4) and 1 mol. (as is usual) to the oxalato-group. The proof now advanced of the existence of complex $[BeOx_2]$ ions suggests an alternative explanation. The solid may consist of the complex salt with the double formula $Be[BeOx_2],6H_2O$. Of these water molecules, four would be attached to the ionised beryllium, and one of the other two to each of the two oxalato-groups. Only an *X*-ray examination of the structure of the crystals could be expected to decide between these two alternatives.

The authors wish to express their thanks to Messrs. Brunner Mond and Co. for a grant towards the expense of this research, and one of them (N.B.L.) to the Commissioners of the Exhibition of 1851 for a scholarship which enabled him to take part in it.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, August 4th*, 1926.]

CCCXXXIV.—*The Spatial Structure of* cyclo*Paraffins. Part II. The Structure of* 1 : 1-*Disubstituted* cyclo*Hexanes.*

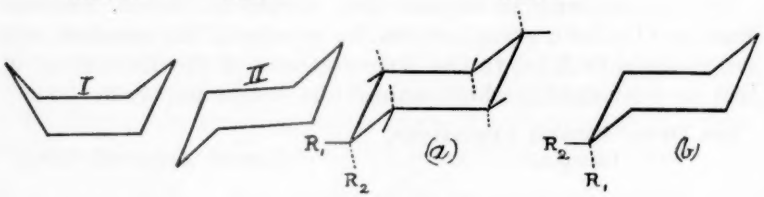
By WILFRED ALAN WIGHTMAN.

IN Part I of this series (J., 1925, **127**, 1421) it was shown that Sachse's strain-free structures for *cyclo*hexane are consistent with the non-existence of isomeric mono-substitution products, because (*a*) relative strain-free rotation of the atoms in type I annihilates isomerism in this form, and (*b*) the interconvertibility (assumed by Mohr) of types I and II by the forces due to molecular collisions removes the need for isomerides corresponding to each. While the first point is proved by the study of suitable models (*loc. cit.*), the second rests on negative evidence only, and instances have recently been found in which it is evidently not applicable, or only partly applicable. The case of di*cyclo*hexyl is of particular significance. Condensation methods using *cyclo*hexyl iodide give a product of b. p. 234—236° (Kursanoff, *J. Russ. Phys. Chem. Soc.*,

1902, **34**, 221; Borsche and Lange, *Ber.*, 1905, **38**, 2769; Hell and Schaal, *Ber.*, 1907, **40**, 4165), while Wallach (*Ber.*, 1907, **40**, 70), by condensing *cyclo*hexanone with itself and reducing the product, obtained a di*cyclo*hexyl, b. p. 227°. Schrauth and Gorig (*Ber.*, 1923, **56**, 1900), by reduction of the products of condensation of *cyclo*hexanol with phenol, obtained three different forms of di*cyclo*hexyl, b. p. 235—237°, 227—228°, and 219·5—221·5°. One of these is stable, whilst the other two are transformed into mixtures of the three by the action of aluminium chloride or of light. Since two of these forms appear to correspond with those previously obtained by other methods, it would seem that we have a clear case of a mono-substitution derivative of *cyclo*hexane existing in more than one form.

Now of Sachse's structures, type I (Fig. 1), by virtue of strainless motion, has all its hydrogen atoms equivalent and is stereochemically indistinguishable from a plane ring. In type II (the rigid form)

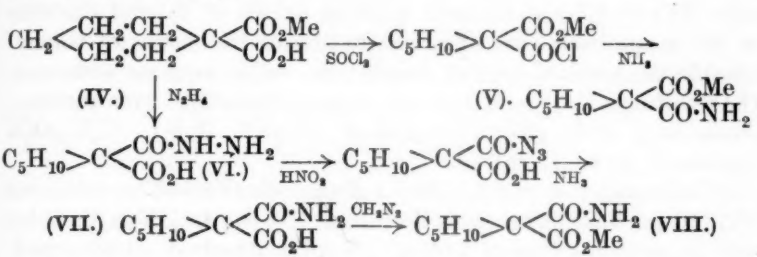
FIG. 1. FIG. 2. FIG. 3.



(Fig. 2), each hydrogen atom is equivalent to its *trans*-neighbours on the adjoining carbon atoms, but not to its *cis*-neighbours or to its partner on its own carbon atom, *i.e.*, the hydrogen atoms fall into two sets of six as indicated in Fig. 3*a*, and this form should give rise to two mono-substituted isomerides. The existence of three di*cyclo*hexyls is thus in accord with the spatial possibilities.

Differences in the stereochemistry of types I and II at once arise. For instance, *cis-cyclo*hexane-1 : 2-dicarboxylic acid can have only one form in the flexible modification, but in the rigid modification it can exist in two forms which are non-superposable mirror images. Attempts to resolve this compound have hitherto failed (Werner and Conrad, *Ber.*, 1899, **32**, 3046; Böeseken and Peek, *Rec. trav. chim.*, 1925, **44**, 841), but Derx (*ibid.*, 1922, **41**, 312) was led to conclude, from experiments on the effect of *cis-cyclo*hexane-diols and *cis*-tetrahydronaphthalenediols on the conductivity of boric acid solutions, that the *cyclo*hexane ring exists in the form of an equilibrium mixture in which type II predominates. It therefore becomes of interest to endeavour to obtain some positive evidence on the spatial structure of simple *cyclo*hexane derivatives.

Fig. 3 shows that if a 1 : 1-disubstituted *cyclo*hexane, $C_6H_{10}R_1R_2$ (*a*), has the rigid structure, then interchange of R_1 and R_2 will give a substance (*b*) which differs from (*a*) and is not its mirror image. If the original substance has the flexible structure, the interchange will make no difference. The present investigation was devised to test this point by carrying through the following series of changes (compare Fischer and Brauns, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **1**, 714).



When this series of operations had been carried out, it was found that the two ester-amides (V) and (VIII), which were solids, m. p. 91·5° and 90—91°, respectively, were identical, giving a mixed m. p. 90—91°.

Positive proof is thus obtained that in this series of derivatives the rigid form of the *cyclo*hexane ring does not exist as a static modification. The possibility of dynamic equilibrium is not, however, excluded.

EXPERIMENTAL.

Dimethyl Ester of cyclo*Hexane*-1 : 1-*dicarboxylic Acid*.—This ester was prepared from pentamethylene dibromide and methyl disodiomalonate in the manner described by Dox and Yoder for the diethyl ester (*J. Amer. Chem. Soc.*, 1921, **43**, 1368). The yield of crude ester (b. p. 110—125°/14 mm. after repeated fractionation) was 22%. It was purified by hydrolysis and re-esterification: colourless liquid, b. p. 119°/14 mm. (Found: C, 59·9; H, 8·0. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

Constitution. Hydrolysis with methyl-alcoholic potash gave *cyclo*hexane-1 : 1-dicarboxylic acid, m. p. 176° (decomp.) (Found: C, 55·3; H, 7·3. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%). On heating to 190°, this substance lost carbon dioxide, giving an acid, m. p. 30·5—31·5°, which proved to be identical with a specimen of hexahydrobenzoic acid prepared from magnesium *cyclo*hexyl bromide and carbon dioxide (mixed m. p. 30—31·5°).

1-*Methyl* 1′-*Hydrogen* cyclo*Hexane*-1 : 1′-*dicarboxylate* (IV).—This substance was prepared by partial hydrolysis of the dimethyl ester

according to Walker's method for acid esters of dialkylmalonic acids (J., 1892, **61**, 710). Acidification of the solution of the potassium salt gave an insoluble oil which solidified when the residue from its dried and evaporated ether solution was kept in a vacuum. It crystallised from low-boiling ligroin in rhombic plates, m. p. 75°, yield 42% (Found: C, 58·1; H, 7·4. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%).

1-*Methyl* 1′-*Carbamyl*cyclo*hexane*-1-*carboxylate* (V).—The acid ester (IV) (3 g.) was refluxed with an excess of thionyl chloride on the steam-bath, and after distillation of the excess of thionyl chloride the residual oil was poured into cooled aqueous ammonia. The resulting white precipitate was twice recrystallised from acetone; prisms, m. p. 91·5°, yield 1·5 g. (Found: C, 57·7; H, 8·1. $C_9H_{15}O_3N$ requires C, 58·4; H, 8·1%).

cyclo*Hexane*-1′-*carboxylic Acid* 1-*Hydrazide* (VI).—The acid ester (IV) (2·1 g.) was shaken with hydrazine (2·6 g., 92% N_2H_4), cooled to 0° in an atmosphere of hydrogen, until it dissolved. After standing for a day at the ordinary temperature, excess of hydrazine was removed in a vacuum at 30°, whereupon the residue solidified to a white, crystalline mass. This was dissolved in water, acidified with acetic acid, and precipitated with lead acetate at 80°. The resulting lead salt was suspended in water and decomposed with hydrogen sulphide at 80°. After thorough extraction of the lead sulphide with hot water, the cooled and concentrated filtrate yielded 1·5 g. of a solid, which on recrystallisation from water gave m. p. 156° (decomp.).

1-*Carbamyl*cyclo*hexane*-1′-*carboxylic Acid* (VII).—Sodium nitrite (0·5 g.) was added to the acid hydrazide (VI) (1 g.) suspended in 15 c.c. of water and ice, and shaken till solution was complete. On acidifying with 5*N*-sulphuric acid the azoimide was precipitated as an oil. This was immediately dissolved in ether and dry ammonia gas was passed into the ether solution cooled in a freezing mixture. A precipitate was formed which, after removal of the ether by suction, was dissolved in water and acidified with hydrochloric acid. Hydrazoic acid was evolved, and the amic acid precipitated. It was recrystallised twice from water, insufficient to dissolve the whole being used; yield, 0·5 g., prisms, m. p. 149° (decomp.) (sintering at 139°).

1′-*Methyl* 1-*Carbamyl*cyclo*hexane*-1′-*carboxylate* (VIII).—The amic acid (VII) was suspended in ether and esterified by addition of diazomethane. The residue after removal of the ether consisted of prismatic crystals similar to (V), m. p. 90—91°, mixed m. p. with (V) 90—91·5°. The identity of the compounds (V) and (VIII) was thus clearly established.

The author wishes to express his thanks to Professor C. K. Ingold, F.R.S., for his kind interest in this work, and to the Research Fund Committee of the Chemical Society for a grant which has largely defrayed the expenses.

THE UNIVERSITY, LEEDS. [*Received, August 8th*, 1926.]

CCCXXXV.—*The Chemistry of Petroleum. Part III. The Acid Sludge from the Refining of Persian Kerosene. Part I. The Aromatic Hydrocarbons.*

By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

IN order to isolate the neutral sulphur compounds from the light distillate (36% by volume) from crude Persian petroleum (J., 1925, **127**, 898) by means of the reaction with alcoholic mercuric chloride, it is first necessary to eliminate hydrogen sulphide and the mercaptans. The former is completely removed by the use of aqueous sodium hydroxide, but the mercaptans are only partly extracted (*loc. cit.*). The oil may be freed from the last traces of mercaptans by repeated agitation with aqueous silver nitrate. A dirty white sludge * is produced, which is very difficult to filter. The small quantities of neutral sulphur compounds present in the petroleum necessitate dealing with a large volume; the process, besides being expensive, is therefore extremely tedious and inconvenient.† Consequently it was decided to make use of the known solubility of the neutral sulphur compounds in concentrated or fuming sulphuric acid. This method offers the advantage that in refinery practice the soda-washed distillate is redistilled, the greater part of the sulphur compounds remaining in the residue (kerosene), which is treated with fuming sulphuric acid; an unlimited supply of acid sludge, from which the required sulphur derivatives could be isolated, was therefore available.

In Part I of this series (*loc. cit.*) it was shown that during the soda-washing of the light distillate a part of the mercaptans is entirely removed, part is converted into disulphides which are left in the oil, and part remains unattacked. The unextracted mercaptans would consist chiefly of the higher (and less acidic) members of

* This may be purified to a white, crystalline powder by recrystallisation from a mixture of acetone and pyridine.

† Both mercaptans and sulphides may be precipitated together by means of mercuric chloride, and a separation attempted later; but neither this procedure nor that outlined above would serve to isolate disulphides, the presence of which was suspected (*vide infra*).

the series, which would remain in the residue on redistillation of the oil. It was therefore to be expected that during a subsequent treatment with sulphuric acid the remaining mercaptans would become oxidised to disulphides, which with those already present would eventually appear in the acid tar; this expectation has been verified in preliminary experiments, since sodium mercaptides are formed by the action of sodium on the oil recovered from acid tar. Since Thierry (J., 1925, **127**, 2756), who isolated a series of sulphides from an acid sludge from the refining of a Persian petroleum, had made no mention of disulphides, the investigation of our acid tar was continued, although Thierry's paper had appeared in the meanwhile.

It was soon found that the oil obtained by diluting the tar from the washing of kerosene with fuming sulphuric acid (20% SO_3) contained, besides sulphur compounds, large quantities of aromatic hydrocarbons, which were investigated.*

Owing to the difficulty of operation on a large scale, on diluting the original black, viscous sludge with water, a certain quantity of kerosene was also admitted. The agitation with acid was therefore repeated, but using 98% acid (dilution of this second tar giving a black oil, rich in the desired sulphur compounds); it was remarkable that the part which remained undissolved, and must have consisted largely of the original kerosene, had a much higher specific gravity than the latter (0·816 compared with 0·793), and still contained 0·5% of sulphur, which was not present in the elementary state. In an endeavour to locate the cause of the high specific gravity and sulphur content, about 87·5% of the material was taken off in a current of steam. The sulphur remained in the residue, but although the distillate now contained only 0·06% of sulphur, it still had d 0·803, which could only be due to the presence of a considerable quantity of aromatic hydrocarbons.

Further concentration of the aromatic constituents was effected by the method of Edeleanu (Brit. Pat., 11140), which consists in dissolving the benzene hydrocarbons in liquid sulphur dioxide; the reagent was used at its boiling point under atmospheric pressure. The extract, after removal of the sulphur dioxide, was fractionally distilled. It commenced to boil at about 60° and fractionation was continued to 220°. Each 5° fraction was separately treated with sulphuric acid (100% H_2SO_4) and the aromatic hydrocarbons were recovered by steam-distilling the acid layer (compare Armstrong

* M. Normand (private communication) suggests that the presence of aromatic hydrocarbons in the acid tar is due to the solvent action of sulphur dioxide, produced by the oxidising action of the acid on the kerosene, dissolved in the acid tar.

and Miller, J., 1884, **45**, 148). Each fraction of recovered hydrocarbon was investigated separately.

The methods recorded in the literature for isolating and identifying the higher aromatic hydrocarbons are surprisingly few and of limited applicability. The use of sulphonic acids has the advantage that the hydrocarbons can be regenerated by hydrolysing the purified acid, but the mixtures of sulphonic acids often fail to crystallise, and criteria of purity for their salts are usually somewhat indirect. The use of nitro-derivatives is unsatisfactory, partly on account of the tarry products formed, partly because they cannot be distilled (thus the methods of separation are limited to crystallisation), and partly because of the difficulty of bringing about complete substitution without the risk of attacking the side chains. If complete substitution is not effected, the formation of isomeric nitro-compounds from the same hydrocarbons introduces a further complication. This difficulty is overcome by replacing every nuclear hydrogen atom by bromine, the resulting bromo-compounds being stable and crystallisable substances, some of which have quite commonly been used for the identification of individual hydrocarbons isolated by other means. Moreover, the use of the brominated compounds provides a valuable, and, so far as we are aware, novel means of accomplishing an actual separation of unknown constituents, since even those bromo-derivatives of highest melting point can be distilled under reduced pressure with but little decomposition. Thus, if a series of hydrocarbon fractions has been isolated, they are exhaustively brominated in the nucleus and the product from each fraction is examined separately. Should a common constituent be found, the proportions in which it occurs in the bromides derived from the different hydrocarbon fractions provide a clue to the boiling point of the original hydrocarbon. This method has proved satisfactory, and is to be recommended for such systematic investigations.

Toluene, *m*-xylene, *p*-xylene, *p*-ethyltoluene, mesitylene, ψ-cumene, hemimellithene, a diethylbenzene, an ethylxylene, and naphthalene were identified; evidence was obtained of the presence of methylnaphthalene.

Careful but unsuccessful search was made for *o*-xylene, which has never, so far as we are aware, been detected in a petroleum, although *m*- and *p*-xylene are quite usual constituents. The presence in Persian oil of mesitylene and ψ-cumene is scarcely surprising, since these hydrocarbons are probably the commonest constituents of liquid petroleums, usually occurring together. Indeed, of all the different petroleums so far investigated, there appear to be only three in which neither mesitylene nor ψ-cumene has been detected—

an oil from Gemsah (Egypt) which gives only 4% of distillate between 160° and 200°, an oil from Kuba in the Caucasus, and a heavy petroleum from Oregon, U.S.A.; in the last two, aromatic constituents have not been found. Neither hemimellithene nor ethylxylene has previously been isolated from a petroleum. Ethyltoluene was suspected, but not identified, by Mabery and Hudson (*Proc. Amer. Acad. Arts Sci.*, 1901, **36**, 259) in the fraction of b. p. 159—163° of an oil from Fresno County, California. Markownikoff (*Annalen*, 1886, **234**, 89) thought that diethylbenzene was probably present in Baku petroleum. Naphthalene and its homologues are quite common constituents of petroleums; we have isolated naphthalene, and β-methyl-, dimethyl-, and trimethyl-naphthalenes (the last two in the form of their picrates) from Persian kerosene by direct extraction with liquid sulphur dioxide, omitting the previous treatment with sulphuric acid.

Experimental.

The starting material was the crude kerosene, left as a residue (12%) when the soda-washed primary distillate from the crude petroleum is redistilled. It is a faintly yellow liquid having $d^{15°}$ 0·793, a sulphur content of 0·19%, and a peculiar odour.

Five thousand gallons of this material were agitated for 45 minutes with 0·75% (by vol.) of fuming sulphuric acid (20% SO_3), and the mixture was allowed to settle during 30 minutes. The viscous, black tar was then allowed to run into water (*ca.* 100 gals.), a certain volume, estimated at 10 gallons, of kerosene being also admitted; the total separated oil, approximately 55 gallons, was then collected and twice extracted with half its volume of concentrated sulphuric acid; the acid gave on dilution a black oil, very rich in sulphur compounds, which was purified by steam distillation. The investigation of this material, which has been shown to contain disulphides by the formation of sodium mercaptides on treatment with sodium, will form the subject of a further communication. The oil which did not dissolve in the sulphuric acid had $d^{15°}$ 0·816 and contained 0·5% of sulphur; it was distilled in steam. The distillate (about 87·5%; $d^{15°}$ 0·803), which contained 0·06% of sulphur, was treated with its own volume of liquid sulphur dioxide in an open separating-funnel, the temperature being allowed to adjust itself automatically by the unchecked ebullition of the reagent (Edeleanu, *loc. cit.*). The heavier sulphur dioxide layer was separated and the solvent removed. The extracted oil, after being washed with aqueous alkali and then with water, was dried over calcium chloride; it had $d^{15°}$ 0·840. This oil was now fractionally distilled, using a 48-inch column packed with iron borings. A few drops of distillate

were collected up to 70°; fractions were then taken at 5° intervals up to 220°.

The extraction with sulphur dioxide, whilst serving to concentrate the aromatic hydrocarbons in the soluble portion, only gives a partial separation; this was therefore completed by treating each of the 5° fractions of the extract with its own volume of concentrated sulphuric acid, the aromatic hydrocarbons being recovered from the acid layer by distillation in steam (compare Armstrong and Miller, *loc. cit.*).

The residue (12·5%) from the large-scale steam distillation was subjected to a separate distillation using superheated steam, which left only a small residue. This second distillate was also treated with liquid sulphur dioxide, the extracted portion distilled, and the fractions up to 220° were treated as before with sulphuric acid, the recovered aromatic hydrocarbons being added to the corresponding fractions from the 87·5% distillate. Fractions boiling above 200° were always distilled with the aid of a lagged, electrically-heated column.

Toluene.—The presence of toluene in the three fractions from 100° to 115° was demonstrated as follows: Nitration gave 2 : 4-dinitrotoluene, m. p. 70—71°. Sulphonation gave *p*-toluenesulphonic acid, m. p. 106°; from this were prepared pure specimens of toluene, b. p. 110·5°, and of *p*-toluenesulphonanilide, m. p. 104°.

m- *and* p-*Xylene.*—The fractions boiling between 130° and 150° were converted into the calcium xylenesulphonates, the solution of which was evaporated in stages, the meta-derivative separating from the hot solution and being collected. From the cold, concentrated solution, the para-salt separated in clusters of large, colourless prisms. These precipitates were then separately purified by fractional crystallisation. The meta-salt was dissolved in cold water and precipitated by heating the solution; the para-salt was dissolved hot and allowed to crystallise by cooling. The hydrocarbons were then regenerated from the calcium sulphonates by heating with sulphuric acid in a current of steam. *m*-Xylene was boiled for 4—5 hours with dilute nitric acid (1 acid : 2 water), washed with aqueous alkali and then with water, dried, and distilled. It had b. p. 141—142° and gave, on bromination,* tetrabromo-*m*-xylene, m. p. 251° (Auwers and Koeckritz, *Annalen*, 1907, **352**, 299, give m. p. 247° (Found: C, 22·8; H, 1·6. Calc.: C, 22·75; H, 1·45%). *p*-Xylene, b. p. 137·5—138°, solidified on cooling, and had m. p. 12—13°. Bromination gave tetrabromo-*p*-xylene, m. p. 252° (Jacobsen, *Ber.*,

* Bromination was always carried out in the dark in the presence of iodine, a large excess of bromine being used (compare Crafts, *Compt. rend.*, 1892, **114**, 110).

1885, **18**, 359, gives m. p. 253°) (Found: C, 22·9; H, 1·5. Calc.: C, 22·75; H, 1·45%).

According to Patterson (J., 1925, **125**, 2489), calcium *o*-xylenesulphonate, being extremely soluble in water, is the last of the isomerides to crystallise on evaporation. The most soluble portion of our calcium xylenesulphonate was carefully examined; eventually this fraction was converted into the sodium salt, which was also examined; from this, in turn, the xylenesulphonamide was prepared and fractionally crystallised, but no ortho-derivative could be detected.

The Trimethylbenzenes and Ethyltoluene.—The three fractions between 155° and 170° each gave on sulphonation a crystalline and an oily acid, which were separated by filtration through glass wool. On being heated with concentrated hydrochloric acid at 100° in a closed vessel (compare Crafts, *Amer. Chem. J.*, 1900, **83**, 248; Armstrong, *Ber.*, 1882, **15**, 1697), both the crystalline and the oily acid gave (*a*) a liquid hydrocarbon, mesitylene, (*b*) crystalline ψ-cumenesulphonic acid, and (*c*) an oily sulphonic acid, which contained a certain quantity of the ψ-cumene acid, and was obtained in greatest amount from the 160—165° fraction.

The oily acid (*c*) was hydrolysed by heating with concentrated sulphuric acid in a current of superheated steam; the hydrocarbon produced was washed, dried, and fractionally distilled. It boiled between 158—168°, with a distinct peak at 162—166°. This peak fraction, which had a peculiar lemon-like odour, was shaken for 6 hours with concentrated sulphuric acid (2 mols.) at the ordinary temperature. The portion which did not dissolve was then treated for 6 hours at 50° with a fresh portion of acid. The hydrocarbon which remained was then brominated; the resulting tetrabromo-*p*-ethyltoluene was washed and dried in light petroleum solution, removal of the solvent then giving a crystalline solid which separated from ethyl alcohol in needles, m. p. 111° (Found: C, 25·0; H, 1·9. Calc.: C, 24·8; H, 1·9%). The somewhat indefinite m. p. of this substance has not hitherto been recorded (compare Klages, *Ber.*, 1903, **36**, 1637), but the identity of our product was established by comparison with a genuine specimen of the synthetic material.

The hydrocarbon (*a*) was again sulphonated; the deliquescent mesitylenesulphonic acid crystallised from chloroform and melted at 77°. A portion of the acid was converted through the sodium salt into mesitylenesulphonamide, which had m. p. 142° after crystallisation from water. Hydrolysis of the acid by heating with sulphuric acid in a current of steam gave mesitylene, b. p. 164°. Bromination of the pure hydrocarbon gave tribromomesitylene, which separated from benzene in needles, m. p. 226° (Fittig and

Storrer, *Annalen*, 1868, **147**, 11, give m. p. 224°) (Found : C, 30·35; H, 2·5. Calc. : C, 30·2; H, 2·55%); the identity of this bromide was confirmed by comparison with a genuine specimen prepared from coal-tar mesitylene.

The crystalline ψ-cumenesulphonic acid (*b*) was purified by repeated crystallisation from dilute sulphuric acid; finally, the material was extracted by means of chloroform in a Soxhlet apparatus, the dry acid, free from sulphuric acid, being obtained in this way. From the same solvent, the acid separated in small, granular crystals, m. p. 110—112°, which were identical with a specimen prepared from genuine coal-tar ψ-cumene. ψ-Cumene was isolated from the acid by distillation with sulphuric acid in a current of steam; it had b. p. 168—169°. Bromination of the pure hydrocarbon gave tribromo-ψ-cumene, m. p. 232° (Jacobsen, *Ber.*, 1886, **19**, 1222, gives m. p. 233°), which was identical with a genuine specimen (Found : C, 30·3; H, 2·6. Calc. : C, 30·2; H, 2·2%).

Fractions 170—175° and 175—180° were refractionated. The portion of b. p. 175—178° was sulphonated and the sulphonic acid converted through the calcium salt into the sodium sulphonate. The aqueous solution of the sodium salt was then treated with less than the theoretical quantity of barium chloride; the precipitated barium sulphonate was reconverted into the sodium salt, and the incomplete precipitation repeated. The process of isolating and collecting the less soluble barium salt was continued until a specimen gave, through the sodium salt and the acid chloride, hemimellithenesulphonamide, m. p. 195° (softening at 192°). Hemimellithene is apparently an important constituent of the aromatic portion of Persian kerosene; it has been isolated in considerable quantity from all the fractions boiling between 175° and 188° as tribromohemimellithene, which is comparatively insoluble in light petroleum or cold ethyl alcohol, but soluble in hot benzene, from which it separates in long needles, m. p. 245° (Jacobsen, *loc. cit.*) (Found : C, 30·6; H, 2·6. Calc. : C, 30·2; H, 2·65%).

Hydrocarbons C_9H_{12} *and* $C_{10}H_{14}$.—The fractions boiling above 175° were refractionated into 2° fractions, which were then brominated. Each fraction up to 188° gave a quantity of tribromohemimellithene (*vide supra*) from which the other products were separated by dissolving them in light petroleum. The soluble portion from fraction 186—188° solidified, and the soluble bromides from the other fractions deposited more of the same solid (A), which was collected. The mother-liquor from each fraction was then fractionally distilled under reduced pressure. From fractions 178—180° and 180—182° there was obtained a fraction of bromo-compound, b. p. 220—230°/9 mm., which solidified (B); the same hydrocarbon

fractions also gave a fraction of bromo-derivative, b. p. 200—220°/9 mm., which deposited a further crop of the solid (A). More of this was also obtained by fractionally distilling the soluble, liquid bromides from the other hydrocarbon fractions.

The solid (A) gave, on crystallisation from ethyl acetate, some tribromohemimellithene and a portion of m. p. 85—95°. From this, tribromoethylxylene was isolated in needles, m. p. 93°, by repeated crystallisation from ethyl acetate, which was occasionally replaced by acetone (Found: C, 32·35; H, 3·0. Calc.: C, 32·35; H, 3·0%). The fact that the soluble bromide (consisting almost entirely of the compound of m. p. 93°) from hydrocarbon fraction 186—188° solidified, seems to indicate that the b. p. of the parent hydrocarbon is very close to that temperature. It is not possible, however, to draw any inference from this, since the b. p.'s of all the known ethylxylenes lie within a very narrow range (185—191°). The m. p. of the tribromo-derivative of 1 : 2-dimethyl-4-ethylbenzene is given as 93° in the literature, whilst for that of 1 : 5-dimethyl-2-ethylbenzene Stahl gives m. p. 94—95°, and Anschütz m. p. 90—91°. Our bromide, m. p. 93°, may, therefore, be derived from either of these ethylxylenes. A sample of bromo-derivative having m. p. *ca.* 106° was also obtained (in very small quantity), and was evidently an isomeric tribromoethylxylene (Found: C, 32·6; H, 3·1%).

Great difficulty was experienced in the purification of the solid (B), the m. p. of which (originally about 48°) was only slightly raised by each crystallisation. After many crystallisations from ethyl acetate or acetone diluted with ethyl alcohol, hard prisms were isolated which still had a rather indefinite m. p., 60—64°. The quantity remaining at this stage was too small to permit of further purification. Nevertheless, the properties of this compound and its composition (Found: C, 26·9; H, 2·4. Calc.: C, 26·7; H, 2·2%) agree with the description of tetrabromo-*o*-diethylbenzene (Voswinckel, *Ber.*, 1888, **21**, 3501), m. p. 64·5°. Since our material was not crystallised "to constant melting point," it is possible, although scarcely probable, that we may have been dealing with an impure specimen of tetrabromo-*m*-diethylbenzene (prisms, m. p. 74°).

Naphthalene.—Treatment of the fraction of b. p. 200—225° with picric acid gave a quantity of picrate, which was freed from the oil as far as possible by pressing on porous porcelain; on heating the picrate with aqueous sodium hydroxide in a current of steam, naphthalene was recovered in the solid form. After crystallisation from ethyl alcohol, it had m. p. 80°, and was identified by means of its picrate, m. p. 151·5° (Found: C, 53·55; H, 3·4. Calc.: C, 53·8; H, 3·1%).

Naphthalene Hydrocarbons in the Sulphur Dioxide Extract.—The fractions boiling above 225° each gave picrates, but the quantities were too small for detailed examination. The deepening of the colour with increase in b. p. of the fractions indicated the presence of homologues of naphthalene (thus, a deep orange picrate, m. p. *ca.* 112°, was obtained from the 250—255° fraction); this was confirmed by a brief investigation of the relevant fractions of the oil extracted from kerosene by means of liquid sulphur dioxide.

The extract, obtained in the normal course of refining kerosene,* was washed with sodium hydroxide solution and the portion boiling up to 200° removed. The brown residue was distilled in steam and the distillate dried and exhaustively treated with picric acid. The collected picrates were freed as far as possible from oil and the hydrocarbons recovered by distillation with steam in the presence of aqueous sodium hydroxide. The heavy, oily distillate was dried and fractionally distilled, 5° fractions being collected.

The fraction of b. p. 215—220° solidified, and, together with the solid deposited on cooling from fractions 220—225° and 225—230°, was collected and identified as naphthalene.

The mother-liquor from these fractions, and the higher fractions (up to 270°), were treated with fuming sulphuric acid (10% SO_3) and the hydrocarbons recovered by steam-distilling the viscous acid layer. The recovered hydrocarbons were washed with sodium hydroxide solution, and dried over calcium chloride. The material was then refractionated.

β-Methylnaphthalene separated from the fraction of b. p. 237—245° on cooling to −21°, and was identified by its m. p. (33°; from alcohol) and its picrate, m. p. 115° (Found: C, 55·0; H, 3·7. Calc.: C, 55·0; H, 3·5%). An attempt was made to separate the mother-liquid (from the β-methylnaphthalene) by fractional crystallisation of the barium sulphonate (Wendt, *J. pr. Chem.*, 1902, **46**, 317). The picrates, prepared from the hydrocarbons recovered from the more soluble and the less soluble portions of the barium salt, were both found to have m. p. *ca.* 120—125°. Attempts to isolate the picrate of α-methylnaphthalene (m. p. 143°) were not successful.

The orange picrate from the dimethylnaphthalene fraction, b. p. 260—265°, was crystallised from ethyl alcohol; it had m. p. 114° (Found: C, 56·0; H, 4·1. Calc.: C, 56·1; H, 3·9%).

A deep orange-red *picrate*, m. p. 119—120°, was obtained from the portion boiling above 270°. Apparently owing to the passage through the combustion apparatus of unburnt hydrocarbon, difficulty was experienced in the analysis of this substance. It is

* In the refinery process, kerosene is agitated at 16° with its own volume of liquid sulphur dioxide; 10% of the oil is dissolved.

evidently the picrate of a trimethylnaphthalene, since it contains too great a proportion of both carbon and hydrogen for the dimethyl derivative (Found: C, 56·6; H, 4·3. Calc. for $C_{18}H_{15}O_7N_3$: C, 56·1; H, 3·9. Calc. for $C_{19}H_{17}O_7N_3$: C, 57·1; H, 4·3%).

Our thanks are due to Prof. J. F. Thorpe, C.B.E., F.R.S., and Drs. A. E. Dunstan and F. B. Thole for their kind interest in the progress of this work, and to Mr. A. M. O'Brien, F.I.C., National Oil Refineries, S. Wales, for kindly affording us facilities for the preparation of our crude material on a large scale.

ANGLO-PERSIAN OIL COMPANY, LTD.,
SUNBURY-ON-THAMES. [*Received, July 12th*, 1926.]

CCCXXXVI.—*The Solubilities of Thallous Chloride in Salt Solutions at 0°, 25°, and 50°, and its Heats of Solution.*

By JOHN ALFRED VALENTINE BUTLER and EDWARD STANLEY HISCOCKS.

THE determination of heats of solution by means of solubility measurements has been the subject of numerous investigations. The familiar van 't Hoff formula $d(\log s)/dt = Q/RT^2$, obtained for ideal solutions, can only be regarded as a rough approximation in the case of electrolytes. Several attempts have been made to obtain the exact relation for such cases: first, by the introduction of the degree of dissociation or the van 't Hoff factor i in various ways (van 't Hoff, *Z. physikal. Chem.*, 1895, **17**, 147; van Laar, *ibid.*, 1895, **17**, 545; 1900, **35**, 11; Goldschmidt and Maarseveen, *ibid.*, 1898, **25**, 91; Jahn, *ibid.*, 1895, **17**, 550; Rudolphi, *ibid.*, 1895, **17**, 277; Campetti, *Atti R. Accad. Lincei*, 1901, **10**, ii, 99; Noyes and Sammet, *J. Amer. Chem. Soc.*, 1898, **20**, 517; Colson, *Compt. rend.*, 1919, **168**, 681), and more recently by Brönsted on the basis of the exact thermodynamics of solutions, in terms of activities (*Z. physikal. Chem.*, 1922, **100**, 139; compare Lange and Dürr, *ibid.*, 1925, **118**, 129). The expression which is now obtained and applied is a modified form of that of Brönsted.

The condition of equilibrium of a salt with its saturated solution may be written $F_s = F_s$, where F_s is the molar free energy of the solid salt and F_s its partial molar free energy in the saturated solution. Now the partial free energy in any solution is given by $F = F_0 + RT \log \alpha$, where α is the activity and $\alpha = \alpha_1\alpha_2$ for a binary electrolyte, α_1 and α_2 being the corresponding activities

of the two ions. Putting $\alpha_1 = \gamma_1 c_1$, $\alpha_2 = \gamma_2 c_2$, where γ_1 and γ_2, c_1 and c_2 are the corresponding activity coefficients and concentrations, respectively, we obtain $F = F_0 + 2RT \log \gamma c^{\pm}$, where $c^{\pm} = \sqrt{c_1 c_2}$ and $\gamma = \sqrt{\gamma_1 \gamma_2}$. The condition of equilibrium may therefore be expressed:

$$\mathrm{F_s} = F_s = F_0 + 2RT \log \gamma_s c_s^{\pm}$$

where $c_s^{\pm}$ is the square root of the solubility product and γ_s the corresponding activity coefficient. Since $\mathrm{F_s}$ and F_0 are constant at a given temperature for a given salt and solvent, $c_s^{\pm} \cdot \gamma_s$ has a constant value for all such saturated solutions, and it will be written $c_s^{0\pm}$.

We shall now apply the equation $d(\mathrm{F}/T)/dT = -\mathrm{H}/T^2$, where H is the heat content corresponding to free energy F, to (1) a very dilute solution of the salt in which the activity coefficient γ is unity, and to (2) the solid salt. In the first case we have

$$F = F_0 + 2RT \log c^{\pm}$$

and

$$d(F/T)/dT = d(F_0/T)/dT = -H_0/T^2$$

since $c^{\pm}$ is not a function of the temperature.*

In the second case,

$$d(\mathrm{F_s}/T)/dT = \mathrm{H_s}/T^2, \text{ whence}$$

$$d\{(\mathrm{F_s} - F_0)/T\}/dT = -(\mathrm{H_s} - H_0)/T^2 = \Delta H_0/T^2.$$

Since

$$\mathrm{F_s} - F_0 = 2RT \log \gamma_s c_s^{\pm} = 2RT \log c_s^{0\pm}$$

we find that

$$d(\log \gamma_s c_s^{\pm})/dT = d \log c_s^{0\pm}/dT = \Delta \mathrm{H_0}/2RT^2 \quad . \quad . \quad (1)$$

$\Delta \mathrm{H_0}$ being the molar heat of solution in a very dilute solution.

A method of finding $c_s^{0\pm}$ has been developed by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112). If the values of $1/c_s^{\pm}$ for a salt in a series of salt solutions be plotted against the ionic strength $\frac{1}{2}\Sigma v^2 c$, where v is the valency of an ion of concentration c and the summation is extended over all the ions present, a series of curves is obtained converging to the value for the pure solvent. When the salt is only slightly soluble, an extrapolation to zero ionic strength can be made with some accuracy, giving the value of $1/c_s^{0\pm}$. The activity coefficient of the salt in any of the solutions is then given by $\gamma = c_s^{\pm}/c_s^{0\pm}$.

* The concentration c is independent of temperature if it expresses the amount of solute per 1000 g. of solvent. In the practical part of the paper concentrations refer to the amount of solute per litre, a quantity which varies slightly with the temperature. The difference is not important for the present purpose.

When such a series of curves has been obtained at two or more temperatures, equation (1) can be applied.

The partial heat of solution in a given solution differs from that in an infinitely dilute solution by the heat of transfer of the salt from the latter to the former. This quantity can be calculated if the temperature coefficient of the activity coefficient in the given solution is known. For, since the free energy of the transfer is $\Delta F = 2RT \log \alpha_1/\alpha_0$ and since $d(\Delta F/T)/dT = -L_1/T^2$, where L_1 is the partial molar change in heat content in the transfer, and $\alpha_1 = \gamma_1 c_1^{\pm}$, $\alpha_0 = c_0^{\pm}$, we have

$$d \log \gamma/dT = -L_1/2RT^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The partial heat of solution of the salt in a given solution is therefore

$$\Delta H = \Delta H_0 + L = 2RT^2 d(\log c_s^{0\pm})/dT - 2RT^2 d(\log \gamma)/dT \quad . \quad (3)$$

Since $\log c_s^{0\pm} = \log c_s^{\pm} + \log \gamma_s$

and $d \log \gamma_s/dT = \{d \log \gamma/dc\}(dc_s/dT) + d \log \gamma/dT$,

(3) reduces to

$$\Delta H = 2RT^2 d(\log c_s^{\pm})/dT + 2RT^2 (d \log \gamma/dc)(dc_s/dT)$$

which is identical with Brönsted's equation.

In practice data for applying (1) and (2) separately are more easily obtained.

Experimental.

Thallous chloride appeared to be a suitable salt for our purpose; its solubilities have already been extensively investigated at 25° (Noyes, *Z. physikal. Chem.*, 1892, **9**, 606; Noyes and Abbot, *ibid.*, 1895, **16**, 130; Geffeken, *ibid.*, 1904, **49**, 271, 296; Bray and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1663) and it seemed desirable on general grounds to extend these measurements to other temperatures. In order to obtain the temperature coefficients entirely from our own data, we repeated some of the earlier determinations; but we took the opportunity to include as solvents some salt solutions not hitherto investigated, particularly lanthanum sulphate, a ter-bivalent electrolyte the solubility influence of which is of some theoretical interest. Solubilities were determined at 0°, 25°, and 50°; the series at 0° and 50° are less comprehensive than that at 25°, first because our analytical method was not suitable for the determination of the low solubilities of thallous chloride in thallous salt solutions at 0°, and, secondly, because we could not obtain concordant values with lanthanum sulphate at 50°, apparently owing to the formation of a compound between the two components.

Materials.—Thallous nitrate was prepared from a commercial

specimen of the salt by treatment with hydrogen sulphide in faintly acid solution, followed by treatment with ammonia and crystallising twice from the filtrate. Thallous sulphate was similarly obtained. Thallous chloride was prepared from the mother-liquors of these preparations by precipitation with pure hydrochloric acid and was twice crystallised from boiling water. It was preserved in a moist condition in blackened resistance-glass vessels. A portion recrystallised twice from conductivity water gave identical solubilities.

Lanthanum sulphate was prepared from a sample of lanthanum ammonium nitrate, kindly put at our disposal by Professor C. M. Thompson, and known to be free from impurities other than traces of cerous salt. The sulphate was obtained from this by way of the carbonate and crystallised twice. [$La_2O_3 : La_2(SO_4)_3$, found : 0·5755. Calc. : 0·5756.]

The other salts employed were of the purest obtainable " Reagent" quality. They were tested and found to be sufficiently pure.

Solubility Determinations.—The solubilities were determined by shaking in a thermostat an excess of thallous chloride with the solution employed as solvent, in special resistance-glass bottles. Sufficient thallous chloride was placed in the bottle and washed with 50 c.c. of the solvent solution. This was rejected and the bottle filled with the same solution and the stopper sealed in with a resin cement and capped. Saturation was approached from both higher and lower temperatures. The solution was withdrawn through a special filter, which could be introduced into the bottle while in the thermostat, and was collected in weighed flasks for analysis.

Methods of Analysis.—Except when thallous salts were used as solvents, the thallium content was determined by titration with potassium permanganate. Our observations confirmed those previously recorded (Noyes, *loc. cit.*; Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300; Berry, *ibid.*, 1922, **44**, 394). We found that a satisfactory end-point could only be obtained in the presence of free hydrochloric acid and when the amount of thallium exceeded 0·9 g. per litre; the requisite quantity of the saturated solution was diluted to 200 c.c. and 14—15 c.c. of concentrated hydrochloric acid added. The permanganate solution was run in at a rate of about one drop per second with vigorous mechanical stirring until a perceptible colour persisted for 3 minutes. Strict adherence to these conditions gave readings reproducible to within 0·3%. The permanganate solution was standardised against pure thallous nitrate. Owing to side reactions the thallium factor so obtained differs from the stoicheiometrical oxygen factor in the ratio 12·588 : 12·750.

TABLE I.

Solubilities of Thallous Chloride in Salt Solutions at 0°, 25°, and 50°.

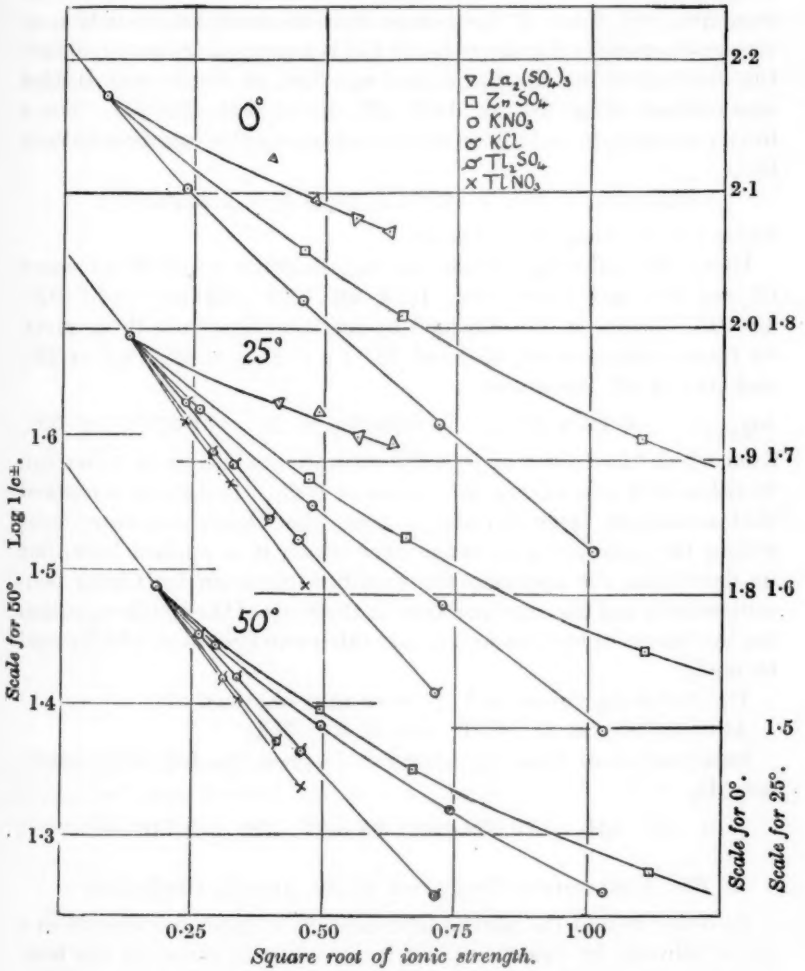
Solvent.	Conc. (mol./ litre).	Solubility. (mol./ litre).	$d_4^{t°}$.	$1/c_s^{\pm}$.	$\mu^{1/2}$.	γ.*
0°						
Water.	—	0·00670	1·0014	149·26	0·08185	0·912
KNO_3.	0·05	0·00787	1·0039	127·07	0·2405	0·776
	0·2	0·00955	1·0155	104·71	0·4578	0·640
	0·5	0·01184	1·0349	84·46	0·7154	0·516
	1·0	0·01472	1·0661	67·93	1·0073	0·415
$ZnSO_4$.	0·05	0·00875	1·0105	114·29	0·4569	0·698
	0·1	0·00979	1·0188	102·14	0·6402	0·624
	0·3	0·01214	1·0674	82·37	1·101	0·503
	0·5994	0·01423	1·1015	70·27	1·553	0·430
$La_2(SO_4)_3$.	0·01	0·00746	1·0063	134·05	0·3968	(0·783)
	0·015	0·00805	1·0088	124·23	0·4827	0·759
	0·02	0·00828	1·0110	120·77	0·5552	0·736
	0·025	0·00845	1·0135	118·34	0·6193	0·722
25°						
Water.	—	0·01607	1·0004	62·23	0·1268	0·863
KCl.	0·05	0·00586	1·0003	55·27	0·2364	0·766
	0·1	0·00387	1·0033	49·88	0·3223	0·692
	0·2	0·00258	1·0063	43·74	0·4501	0·606
	0·5	0·00176	1·0203	33·65	0·7084	0·467
$TlNO_3$.	0·05	0·00615	1·0079	53·82	0·2370	0·746
	0·1	0·00413	1·0202	48·22	0·3227	0·668
	0·2	0·00300	1·0399	40·52	0·4506	0·562
Tl_2SO_4.	0·025	0·00680	1·0098	50·88	0·2861	0·706
	0·05	0·00463	1·0186	45·43	0·3933	0·629
KNO_3.	0·05	0·01826	1·0038	54·76	0·2613	0·759
	0·2	0·02151	1·0138	46·49	0·4706	0·645
	0·5	0·02556	1·0327	39·12	0·7250	0·542
	1·0	0·03030	1·0619	33·00	1·0257	0·458
$ZnSO_4$.	0·05	0·01801	1·0097	48·57	0·4697	0·673
	0·1	0·01836	1·0184	43·88	0·6502	0·608
	0·3	0·01913	1·0515	36·10	1·1080	0·500
	0·5994	0·01937	1·0993	31·22	1·5588	0·432
$La_2(SO_4)_3$.	0·01	0·01801	1·0055	55·52	0·4099	(0·766)
	0·015	0·01836	1·0079	54·46	0·4933	(0·747)
	0·02	0·01913	1·0098	52·27	0·5649	(0·731)
	0·025	0·01937	1·0122	51·63	0·6280	0·716
50°						
Water.	—	0·03265	0·9950	30·63	0·1807	0·803
KCl.	0·05	0·01835	0·9943	28·24	0·2614	0·741
	0·1	0·01281	0·9957	26·31	0·3358	0·688
	0·2	0·00893	0·9996	23·15	0·4571	0·607
	0·5	0·00606	1·0121	18·06	0·7714	0·474
$TlNO_3$.	0·1	0·01381	1·0131	25·22	0·3374	0·662
	0·2	0·01010	1·0321	21·71	0·4584	0·569
Tl_2SO_4.	0·025	0·02061	1·0012	26·21	0·3092	0·688
	0·05	0·01567	1·0140	23·52	0·4070	0·617
KNO_3.	0·05	0·03598	0·9989	27·79	0·2932	0·729
	0·2	0·04136	1·0088	24·18	0·4913	0·634
	0·5	0·04794	1·0273	20·86	0·7402	0·547
	1·0	0·05524	1·0571	18·10	1·0273	0·475
$ZnSO_4$.	0·05	0·04027	1·0046	24·83	0·4902	0·651
	0·1	0·04457	1·0249	22·44	0·6668	0·589
	0·3	0·05349	1·0459	18·70	1·1196	0·490
	0·5994	0·06163	1·0952	16·23	1·5682	0·426

* Figures in brackets are smoothed values obtained from the curves. In other cases the smoothed curve coincides with the experimental points.

In the thallium salt solutions the amount of chloride was determined by precipitation and weighing as silver chloride.

The solubilities are collected in Table I, together with the calculated values of $1/c_s^{\pm}$ and the ionic strengths (μ) of the

FIG. 1.



solutions. Usually four determinations were made in each case and the maximum deviation from the mean was rarely more than 0·00002. The solubilities agree moderately well with the determinations of Bray and Winninghoff (*loc. cit.*), but the divergencies are greater than those of our own determinations among themselves;

they are less than 0·00010, except in the case of *N*-potassium nitrate, where the discrepancy is 0·00042. Considering the difficult nature of the end-point on which the values depend this is perhaps to be expected. In Fig. 1 the values of $1/c_s^{\pm}$ are plotted against the square roots of the ionic strengths, giving a group of curves converging to the value for water for each temperature. It will be seen from the form of the curves that accurate extrapolation to zero ionic strength for the value of $1/c_s^0$ is not possible, and to obtain this limiting value the theoretical equation of Debye and Hückel was utilised (*Physikal. Z.*, 1923, **24**, 185; 1924, **25**, 97). For a binary electrolyte and for small concentrations this equation reduces to

$$\log_{10}\gamma = -7{\cdot}77 \times 10^{15}\sqrt{2\mu}/\{\sqrt{1000} \times 1{\cdot}982(\varepsilon T)^{3/2}\}$$

where ε is the dielectric constant.

Using the following values for the dielectric constant of water (Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1098; Baxter, *ibid.*, 1926, **48**, 615. Value at 50° obtained by interpolation from those given by these authors at 0°, 25°, and 75°): $\varepsilon = 87{\cdot}8$ at 0°, 78·8 at 25°, and 70·7 at 50°, we obtain

$\log_{10}\gamma = -0{\cdot}489\sqrt{\mu}$ at 0°; $-0{\cdot}505\sqrt{\mu}$ at 25°; $-0{\cdot}526\sqrt{\mu}$ at 50°,

from which the values of γ in the saturated solutions in water can be calculated and thence the values of $1/c_s^{0\pm}$. It may be remarked that somewhat large deviations from the Debye equation occur within the concentration range over which it is applied here, but no data exist for applying the modified equation for higher concentrations, and the extrapolation on the basis of the simple equation fits the curves at least as well as any other extrapolation which could be made.

The following values of $1/c_s^{0\pm}$ were thus obtained: *

At 0°, 163·6; at 25°, 72·1; and at 50°, 38·1.

Substitution of these in equation (1) gives the following values for ΔH_0:

$$0\text{—}25°,\ \Delta H_0 = 10{,}560 \text{ cals.};\quad 25\text{—}50°,\ \Delta H_0 = 9{,}740 \text{ cals.}$$

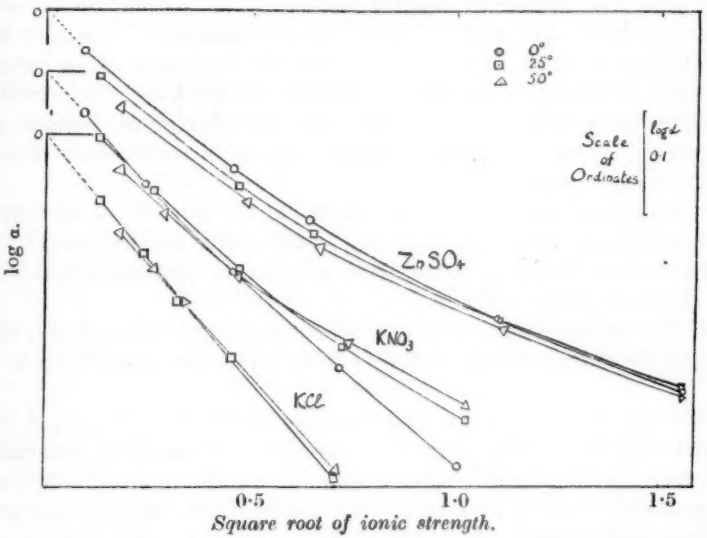
The Temperature Coefficients of the Activity Coefficients.

In order to find the partial heat content of thallous chloride in a given solution by equation (2) it is necessary to ascertain the tem-

* The value of $1/c_s^{0\pm}$ obtained by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1139) by direct extrapolation of the plot of $1/c_s^{\pm}$ against $\mu^{1/2}$ was 70·3 at 25°. Theoretically, at small dilutions $\log 1/c_s^{\pm}$ is proportional to $\mu^{1/2}$, but plotting these quantities brings out differences in the slopes of the curves which are suppressed by the other method. Hence we did not feel justified in attempting a direct extrapolation.

perature coefficient of the activity coefficient in that solution. The solubility method gives directly the activity coefficients in a series of saturated solutions which differ in the content of thallous chloride at different temperatures. It was thought that the true temperature coefficient for a solution would be given by taking values *at the same ionic strength* on the solubility curves. An examination of these showed, however, that the deviations from the ionic-strength rule were so great even at small dilutions that the temperature coefficient for constant ionic strength on the solubility curves could not be identified with that of a given solution. We were therefore unable to apply equation (2).

FIG. 2.



The effect of temperature on the activity coefficient–ionic strength curves of some typical series is shown in Fig. 2, which gives a general idea of the magnitude of the effect.

Conclusions.

The data obtainable from solubility measurements are thus not by any means ideal for the thermodynamical calculation of heats of solution. Equation (1) can only be applied to solubility measurements through an extrapolation to zero-concentration. In the present instance, we were obliged to make use of a theoretical extrapolation which is probably not exact. The use of equation (1) demands a knowledge of (*a*) the solubilities, and (*b*) the activity coefficients in the saturated solutions of a salt, at different tem-

peratures. The latter quantities are better obtained by direct determinations of the activities over a range extending from very low concentrations up to the saturated solution. Data for the application of equation (2) would also be better obtained from direct determinations of activity coefficients in the same solution at two or more temperatures.

Summary.

1. A relation is obtained between the heats of solution and the temperature coefficient of solubility which, though equivalent to one deduced by Brönsted, can be more easily applied to experimental data.

2. The solubilities of thallous chloride in a number of salt solutions at 0°, 25°, and 50° have been determined. The activity coefficients in these solutions are obtained by means of an extrapolation based on the equation of Debye and Hückel. The activity coefficients in solutions of the ter-bivalent electrolyte, lanthanum sulphate, deviate somewhat widely from the requirements of the ionic-strength rule.

3. Values of $1/c_s^{0\pm}$ (*i.e.*, the reciprocal of the theoretical solubility in a solution of zero ionic strength) at the above temperatures have led to values for ΔH_0, the heat of solution of thallous chloride in an infinitely dilute solution.

4. The temperature coefficient of the activity coefficient of a salt cannot be obtained with certainty from solubility measurements.

We wish to express our indebtedness to Mr. Roy Evans, B.Sc., and to Mr. S. O. Rees, B.Sc., for carrying out solubility determinations in lanthanum sulphate solutions and in thallous salt solutions, respectively, and to Professor J. E. Coates, D.Sc., for facilities provided for this work.

UNIVERSITY COLLEGE OF SWANSEA. [*Received, June 30th,* 1926.]

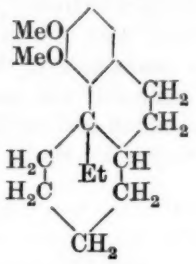
CCCXXXVII.—*Degradative Experiments in the Morphine Group.*

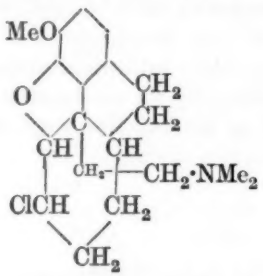
By ROBERT SIDNEY CAHN.

THE present experiments were instituted with the object of preparing degradation products of the natural alkaloids of the morphine group, which, while retaining an unmodified carbon skeleton, should yet be of as simple a character as possible. It appears that further progress in our knowledge of the structural chemistry of these bases

can only be made as a result of definite synthesis of such derivatives. With this end in view, attempts to prepare the substance having the formula (I) * were made, a study of the literature having shown that feasible routes to the compound had been indicated by other workers. For example, Speyer and Koulen (*Annalen*, 1924,

(I.)

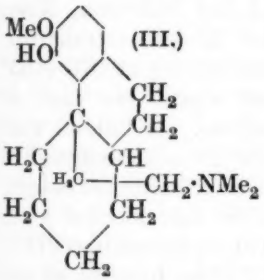




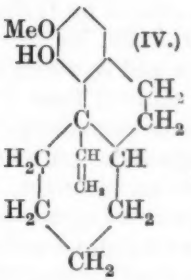
(II.)

438, 34) found that tetrahydro-α-methylmorphimethine (obtained by catalytic reduction of α- or β-methylmorphimethine) on treatment with phosphorus pentachloride gave the chloro-compound (II), which was reduced by sodium and alcohol to a base, m. p. 161—163°, to which they assigned the constitution (III) (dihydrodeoxytetrahydro-α-methylmorphimethine); the methiodide of this very readily lost trimethylamine on boiling with alkali and gave a substance, m. p. 76—78°, which they believed to be (IV), whilst by means of methyl sulphate the phenolic hydroxyl group was methylated and the dimethoxy-base (V) isolated as methiodide. If these results could be substantiated, it is clear that the substance (I) could be

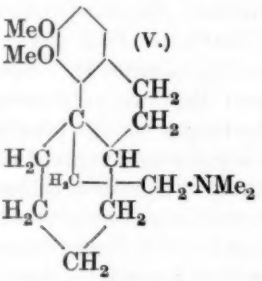
(III.)



(IV.)



(V.)



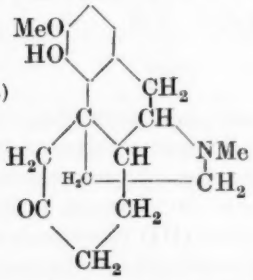
prepared from (IV) by reduction followed by methylation, or alternatively from the methiodide of (V) by Hofmann degradation followed by reduction. On examination, however, it was found that the nitrogen-free compound, contrary to the statement of Speyer and Koulen, is insoluble in alkali, and, as it can be neither methylated

* In the formulæ in this paper the attachment of the ethanamine chain to C^{13} (Gulland and Robinson, J., 1923, **123**, 980) is assumed, and the constitutions of all compounds are modified where necessary in this respect.

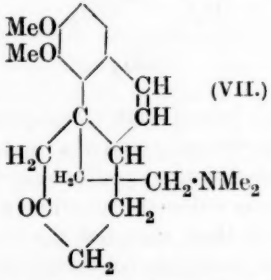
nor acetylated, it must contain, not a phenolic hydroxyl group as in (IV), but rather an ether linking as in thebenol, thebenone, etc. Further, the dimethoxy-methiodide on heating with amyl-alcoholic potassium hydroxide loses, not trimethylamine, but one methyl group, and gives a nearly quantitative yield of the dimethoxy-base, an oil characterised by various well-defined derivatives.

Gulland and Robinson (J., 1923, **123**, 988) treated dihydrothebainone (VI) with diazomethane and characterised the methylated product by its methiodide. The same salt was more readily obtained by methylation with methyl sulphate and on boiling with alkali gave the methine (VII). The double bond at the 9 : 10-position

(VI.)



(VII.)



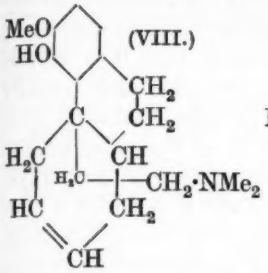
was reduced catalytically and the *dihydromethyldihydrothebainone-methine* * thus obtained yielded on reduction by Clemmensen's method an oily base to which formula (V) must be assigned, but which was *not* identical with that obtained from Speyer and Koulen's series. This difference was not due to possible *cis–trans* ring isomerism (the explanation offered by Gulland and Robinson, *Mem. Manchester Phil. Soc.*, 1925, **69**, No. 10, for the two tetrahydrodeoxycodeines †). Speyer and Koulen's base melting at 161—163° and the two substances derived from it all absorb one mol. of hydrogen in the presence of colloidal palladium. It follows that they are unsaturated compounds and that the formulæ assigned to them by Speyer and Koulen are incorrect. The reduction of chlorotetrahydro-α-methylmorphimethine by sodium and alcohol leads not to (III), but to deoxytetrahydro-α-methylmorphimethine (VIII), which contains a double bond in ring III.‡ The formula of the nitrogen-free compound, m. p. 76—78°, is accordingly (IX) (a five-

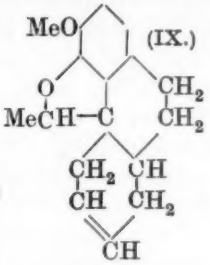
* It seems preferable to extend the "methine" nomenclature to this series (compare Gulland and Robinson, J., 1923, **123**, 985) rather than to adopt the "de-*N*-methyl" method of many German chemists (see footnote, p. 2570).

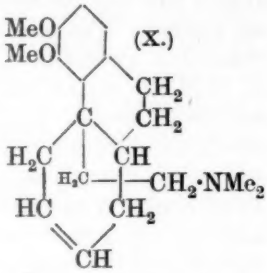
† Some additional work on these compounds is reported in the experimental part of this paper.

‡ The position 6 : 7 chosen for the double bond seems preferable to 5 : 6, which is, however, also possible.

membered oxygen ring being adopted here in preference to the six-membered ring hitherto assigned to these compounds), and that of







the dimethoxy-base obtained from Speyer and Koulen's methiodide is (X). The catalytic reduction of (X) did not proceed to completion owing to the impossibility of obtaining the oily substance sufficiently pure, and the nitrogen-free compound (IX) gave an oil. The base (VIII), however, yielded a crystalline substance to which formula (III) applies; the methiodide of this loses trimethylamine on heating with aqueous alkali and gives an oily nitrogen-free compound, doubtless identical with that obtained by reduction of the substance (IX); and finally, if this reduced base (III) is methylated with methyl sulphate and the quaternary salt thus obtained heated with amyl-alcoholic potassium hydroxide, one methyl group is lost and a dimethoxy-base (V) obtained, which is different from that obtained from Speyer and Koulen's methiodide and appears to be identical with that obtained from the dihydrothebainone series.

Experimental.

Deoxytetrahydro-α-methylmorphimethine (VIII), obtained according to Speyer and Koulen's directions (*loc. cit.*) and recrystallised from chlorobenzene, melted at 163—164°. The *perchlorate*, crystallised from water, melted at 159°. The methiodide lost trimethylamine, on heating with aqueous potassium hydroxide, with a readiness which is seldom met with in this group of compounds unless an ether linking is formed with the phenolic 4-hydroxyl group; the nitrogen-free compound (IX) thus obtained was recrystallised from a little alcohol and had m. p. 79—81°. This is the only one of these compounds which was erroneously analysed by Speyer and Koulen; in the others, the deficiency of two hydrogen atoms cannot be detected with certainty, although indications were in all cases obtained. Speyer and Koulen's figures (C, 78·2, 78·3; H, 8·1, 8·0%) agree better with the formula $C_{15}H_{18}O_2$ (C, 78·2; H, 7·9%) than with the correct formula $C_{15}H_{16}O_2$ (C, 78·9; H, 7·1%), whilst the values obtained in the present investigation (C, 79·0, 79·2; H, 8·0,

8·0%) are inconclusive. Nevertheless, the reactions now described leave no doubt as to the correct constitution (IX) and it would appear that the low-melting substance is difficult to free from adhering solvent. The substance is insoluble in dilute aqueous sodium or potassium hydroxide. Speyer and Koulen state that it is soluble in alcoholic potassium hydroxide; it is, however, fairly readily soluble in alcohol, and addition of a drop of alkali solution to a saturated alcoholic solution containing a little of the substance in suspension did not cause a further appreciable quantity to dissolve. In attempts to acetylate it by heating on the steam-bath for 1 hour with ten times its weight of acetic anhydride, or to methylate it by (*a*) allowing it to stand over-night with methyl sulphate in aqueous-alcoholic sodium hydroxide solution, (*b*) refluxing it in benzene for 2 hours with excess of methyl iodide and silver oxide, and (*c*) refluxing it for 2 hours in nitrobenzene with excess of methyl sulphate and potassium carbonate, the unchanged substance was in all cases isolated almost quantitatively. For the reduction of the double bond in ring III, a palladinised charcoal catalyst was prepared by stirring a suspension of norite (2 g.) in a solution of palladous chloride (0·2 g.) in water (100 c.c.) in the presence of hydrogen until absorption ceased, filtering, and washing with water and finally with alcohol. This catalyst was added to a solution of the substance (IX) (1 g.) in alcohol (35 c.c.), which then, on being stirred in an atmosphere of hydrogen, absorbed 112 c.c. (corrected to *N.T.P.*) in 25 minutes. In a blank experiment the recovered catalyst adsorbed 15 c.c.; the real absorption was thus 97 c.c. (1 mol. = 87 c.c.). After the reduction, the solution was filtered hot and evaporated to dryness, whereby a colourless oil was obtained which could not be crystallised. Seeding with the original substance was without effect.

Methyldeoxytetrahydro-α-methylmorphimethine (X).—The methiodide (2·8 g.) of this compound (Speyer and Koulen, *loc. cit.*) was refluxed in amyl alcohol (30 c.c.) with potassium hydroxide (5 g.) for 2½ hours. The alcohol was removed by steam-distillation and the oil taken up in ether and shaken with dilute acid. The ethereal solution after drying over calcium chloride gave on evaporation a minute quantity of a yellow oil. The acid solution was treated with excess of ammonia and the base was extracted by ether, dried over potassium carbonate, and obtained after evaporation as an almost colourless oil (yield 1·7 g.; 85%). It was identified as *methyldeoxytetrahydro-α-methylmorphimethine* by its methiodide, which was readily formed on treatment with methyl iodide and could be recrystallised from water or from acetone–ether; it melted at 209—211° after sintering at 208° and at the same temperature when mixed with the original methiodide used for the degradation. The

hydriodide separates from water, in which it is very sparingly soluble in the cold, in felted needles and short columns, m. p. 170—171° (Found, in material dried at 100° in a vacuum : C, 54·25; H, 6·85; I, 28·3; MeO, 13·5. $C_{20}H_{30}O_2NI$ requires C, 54·15; H, 6·8; I, 28·6; 2MeO, 14·0%). The *perchlorate* separates from water in needles, m. p. 206—208°. The base dissolves in concentrated sulphuric acid with a not very intense reddish-orange coloration which soon disappears on dilution.

Dihydrodeoxytetrahydro-α-methylmorphimethine (III).—A solution of deoxytetrahydro-α-methylmorphimethine (3·5 g.; m. p. 163—164°) in 1% acetic acid solution (100 c.c.), on being stirred with hydrogen in the presence of the colloidal palladium derived from 20 c.c. of standard catalyst solution,* absorbed 272 c.c. (corrected to *N.T.P.*) in 70 minutes (1 mol. = 258 c.c.). After flocculation of the colloid and filtration, *dihydrodeoxytetrahydro-α-methylmorphimethine* (3·2 g.) was precipitated by ammonia as a colourless, microcrystalline powder, which separated from chlorobenzene in rods, m. p. 152·5—154° (Found, in material dried at 100° : C, 75·2; H, 9·7. $C_{19}H_{29}O_2N$ requires C, 75·2; H, 9·6%). It is somewhat more soluble in chlorobenzene than the unreduced compound. A satisfactory depression of m. p. could not be obtained after mixing it with the unreduced base; when approximately equal quantities were either mixed on a porous plate or melted together on a watch-glass and allowed to resolidify, the m. p. was 148—151° after slight previous sintering. The *hydriodide* of the new base separates from water in rectangular columns and irregular plates, m. p. 219—220°, whereas that of the unreduced base could not be crystallised and is also not recorded by Speyer and Koulen. The *perchlorate* separates from water in rods, m. p. 150—153°. The *methiodide* was gradually precipitated as a crystalline powder on warming a solution of the base in ethyl acetate with methyl iodide, m. p. 230° (Found, in material dried at 100° in a vacuum : I, 28·5. $C_{20}H_{32}O_2NI$ requires I, 28·5%). To a solution of this methiodide (0·7 g.) in boiling water (2·5 c.c.) was added 50% potassium hydroxide solution (5 c.c.), whereupon precipitation of an oil and rapid evolution of trimethylamine took place. The reaction was completed by boiling the solution for 5 minutes; the oil was purified but could not be crystallised. Seeding with Speyer and Koulen's substance (IX) was without effect and it is highly probable that this oil is identical with that obtained by reduction of the substance (IX).

Methyldihydrodeoxytetrahydro-α-methylmorphimethine (V). —*Method A*. Dihydrodeoxytetrahydro-α-methylmorphimethine (2·3

* This solution contained 0·5% of palladous chloride and 0·5% of gum arabic in water.

g.) was shaken with 8% sodium hydroxide solution (in which this phenolic base does not dissolve), and methyl sulphate (7·5 c.c.) gradually added with cooling, shaking being continued until the whole was homogeneous. Addition of potassium iodide solution to a portion of this solution precipitated an oily methiodide, which could not be induced to crystallise, and seeding with the methiodide of dihydrodeoxytetrahydro-α-methylmorphimethine and with that of methyldeoxytetrahydro-α-methylmorphimethine was without effect (the former to indicate whether methylation had taken place, the latter to confirm the reduction). To the bulk of the solution was added 50% potassium hydroxide solution (75 c.c.) and the whole refluxed for 2 hours, whereupon a dark oil rapidly separated; this consisted of the methosulphate, which was stable to boiling aqueous alkali, for at the end of this time ether extracted only a negligible quantity of material, either neutral or basic. The solution was then treated with solid potassium hydroxide, and the supernatant oil dissolved in amyl alcohol (15 c.c.). Potassium hydroxide (5 g.) was added to the alcoholic solution, which was refluxed for 2 hours; the amyl alcohol was then removed by distillation in steam and the residual solution extracted with ether. The extract was shaken with dilute acid and then retained only a negligible amount of neutral material. *Methyldihydrodeoxytetrahydro-α-methylmorphimethine* was extracted by ether from the acid solution after addition of ammonia, dried over potassium carbonate, and obtained on removal of the solvent as a nearly colourless oil (yield 1·8 g.; 78%). The *hydriodide*, after two recrystallisations from water, melted at 174—176°; mixed with that of methyldeoxytetrahydro-α-methylmorphimethine (m. p. 170—171°), it sintered at 153° and melted unsharply at *ca.* 155—158°. The *methiodide* could not be crystallised. The *perchlorate* after recrystallisation from water melted at 194—195°; mixed with the perchlorate of methyldeoxytetrahydro-α-methylmorphimethine (m. p. 206—208°), it melted unsharply over the range 195—206°, even when the substances had been melted together on a watch-glass and allowed to resolidify. The depression obtained with the hydriodides, however, leaves no doubt that these two substances are different.

Methyldihydrothebainonemethine (VII). — Dihydrothebainone * (18 g.) was shaken with 10% sodium hydroxide solution (180 c.c.), the base going into solution and separating later as a paste of

* Freed from dihydrothebaine, which always accompanied the phenolic base in the reduction product of thebaine, by solution in alkali and precipitation by carbon dioxide. The crystalline base thus obtained melted at 140—150°, being contaminated with dihydrothebainol (Skita, *Ber.*, 1921, **54**, 1560), but was pure enough for further work.

crystalline sodium salt. Methyl sulphate (15 c.c.) was added in portions with shaking until a clear red solution was formed. Addition of a concentrated solution of potassium iodide (20 g.) precipitated the methiodide of methyldihydrothebainone as a rapidly solidifying oil which, after standing for 1 hour, was collected in a glass Gooch crucible and drained. A portion, recrystallised from methyl alcohol, melted at 258—260° (decomp.) after darkening at *ca.* 255°. Gulland and Robinson (J., 1923, **123**, 1009) prepared this compound by a different method and state that it darkens slightly at 257—258°. The crude methiodide was dissolved in boiling water (180 c.c.), 10% sodium hydroxide solution added, and boiling continued for 10 minutes. The deposited oil was cooled, taken up in ether, and dried over potassium carbonate. On removal of the solvent, *methyldihydrothebainonemethine* was obtained as a pink oil which solidified on cooling. It is very soluble in ethyl and methyl alcohols and in benzene, slightly less soluble in ethyl acetate, insoluble in dilute sodium hydroxide solution, although appreciably soluble in water, from which it is precipitated by strong alkali. It is best purified by distillation in a high vacuum (b. p. 184—186°/2 mm.), being obtained as a colourless, very viscous oil, which slowly solidifies and is pure enough for further work. On recrystallisation from ligroin, it melts at 89·5° (Found: C, 72·65; H, 8·2. $C_{20}H_{27}O_3N$ requires C, 72·9; H, 8·2%) (yield of distilled product, 12 g.; 61%). The *hydriodide* separates from water in columns, m. p. 211—212° (Found: I, 27·7. $C_{20}H_{28}O_3NI$ requires I, 27·8%). The *semicarbazone* was prepared by warming the base (0·5 g.) with sodium acetate (2 g.) and semicarbazide hydrochloride (1 g.) in dilute acetic acid (10 c.c.) for 5 minutes at 80°, cooling the mixture, keeping it for 5 minutes, rendering it alkaline with sodium carbonate, and extracting it with chloroform. The oil left on removal of the solvent crystallised on being rubbed with alcohol and separated from this solvent in needles, m. p. 184° (Found: N, 13·8. $C_{20}H_{30}O_3N_4,H_2O$ requires N, 13·9%). On allowing the base (0·5 g.) to stand for 70 hours with a solution of potassium hydroxide (0·2 g.) and piperonal (0·5 g.) in alcohol (10 c.c.), a yellow colour was developed, and the *monopiperonylidene* derivative was obtained in the usual way, as a yellow oil, which gave with concentrated sulphuric acid a deep yellowish-red solution becoming colourless on slight dilution. No attempt was made to prepare a dipiperonylidene derivative. The *methiodide* was readily formed as a red oil on gently warming the base with 1 part each of methyl alcohol and methyl iodide and evaporating the mixture. A portion slowly crystallised after several days; recrystallised from a minimum of methyl alcohol and dried in a vacuum at 100°, it melted at *ca.* 189°, but was not quite pure.

Attempts to degrade this methiodide (*a*) by heating with aqueous sodium hydroxide solution, (*b*) by transformation into the quaternary hydroxide by means of silver oxide and heating this for several hours on the steam-bath or for 30 minutes at 200°, and (*c*) by transformation into the methochloride and reduction of this by 5% sodium amalgam, were all unsuccessful. By the last method, a very small quantity of a neutral substance, m. p. 138—141°, was obtained but it was not further investigated.

Dihydromethyldihydrothebainonemethine.—A solution of methyldihydrothebainonemethine (12 g., distilled) in 4% acetic acid solution (120 c.c.), on being stirred with hydrogen in the presence of colloidal palladium (from 20 c.c. of standard catalyst solution), absorbed 790 c.c. (corrected to *N.T.P.*) in 17 minutes (1 mol. = 820 c.c.). After flocculation of the colloid and filtration, the base was rendered to ether after addition of ammonia and dried over potassium carbonate. On removal of the solvent, *dihydromethyldihydrothebainonemethine* (11·5 g.) was obtained as a colourless oil which rapidly solidified. It is very soluble in ether and ethyl and methyl alcohols. Recrystallised from light petroleum, it melts at 70·5—72° (Found: C, 72·8; H, 9·1. $C_{20}H_{29}O_3N$ requires C, 72·5; H, 8·85%). Mixed with the unreduced base, it melted at 57—59°, but equal quantities melted together on a watch-glass could not be induced to crystallise on cooling. The *hydriodide* separates from water in needles, m. p. 224—225° (Found: I, 27·7. $C_{20}H_{30}O_3NI$ requires I, 27·6%); the *perchlorate* melts at 216°. The *semicarbazone* was obtained as a gum which slowly crystallised. Recrystallised from alcohol, it melted at 176—178° (Found: N, 13·5, 13·6. $C_{21}H_{32}O_3N_4,H_2O$ requires N, 13·8%). On boiling a methyl-alcoholic solution of the base for a few minutes with excess of methyl iodide and subsequently removing the solvents, the methiodide was obtained as an uncrystallisable oil, which set to a glass on cooling. It is very soluble in water and alcohol; addition of sodium acetate and perchloric acid to its solution in water precipitates the *methoperchlorate*, which crystallises from water in needles, m. p. 185—186°. The same salt can also be prepared from *dihydro-dihydrothebainonemethine.** This base was prepared in several ways by Wieland and Kotake (*Annalen*, 1925, **444**, 89), who gave m. p. 154—156°. The present author prepared it according to their directions by catalytic reduction of dihydrothebainemethine, but in two separate experiments the highest m. p. which could be obtained was 138—139°. The substance was identified by its picrate, m. p. 185—187° (Wieland and Kotake, 185—188°), and by conversion into thebenone, m. p.

* Wieland and Kotake (*loc. cit.*), adopting the German notation (see footnote, p. 2564), call this "dihydrode-*N*-methyldihydrothebainone."

134—137°. Wieland and Kotake report that this phenolic base is very difficult to methylate, but this observation has not been confirmed. Dihydro-dihydrothebainonemethine (5 g.) was shaken with 2*N*-sodium hydroxide solution, and methyl sulphate (14 c.c.) added in small portions with cooling, shaking being continued until a homogeneous liquid was obtained. Addition of perchloric acid precipitated the *methoperchlorate* of *dihydromethyldihydrothebainonemethine*, which separated from alcohol in needles, m. p. 185° (yield 5 g.; 71%). No depression of m. p. was observed with a mixture with the same salt obtained by the alternative method given above. For comparison, the *perchlorate* of *dihydro-dihydrothebainonemethine* was prepared; it separated from water in long, thin needles, m. p. 233°.

Methyldihydrodeoxytetrahydro - α - methylmorphimethine (V).—*Method B.* Dihydromethyldihydrothebainonemethine (4 g.) in 17% hydrochloric acid (100 c.c.) was heated on the steam-bath with amalgamated zinc turnings (40 g.); after 1 hour more of the acid was added from time to time to maintain a brisk evolution of hydrogen; after 3½ hours, during which time an oil gradually separated and later solidified (probably the hydrochloride or zinc double salt), the solution was cooled and treated with an excess of ammonia. Two extractions with ether removed the *methyldihydrodeoxytetrahydro-α-methylmorphimethine*, which was obtained, after drying over potassium carbonate and evaporation of the solvent, as a colourless, uncrystallisable oil (3·5 g.). The *hydriodide*, recrystallised twice from water, formed needles, m. p. 177·5—178·5° (Found in material dried at 100° in a vacuum: C, 54·1, 54·3; H, 7·4, 7·4; I, 28·5; MeO, 14·0. $C_{20}H_{32}O_2NI$ requires C, 53·9; H, 7·25; I, 28·5; 2MeO, 13·9%). Mixed with the hydriodide of methyldeoxytetrahydro-α-methylmorphimethine, it melted at 153—156°; mixed with the hydriodide (m. p. 174—176°) of the base obtained by method A, it melted at 175—177°. The perchlorate, after one recrystallisation from water, melted at 184—185°, and after a second, at 190—191°. Mixed with the perchlorate (m. p. 194—195°) of the base prepared by method A, it melted at 191—193°. On gently warming the base (1 g.) with methyl alcohol (2 c.c.) and methyl iodide (2 c.c.) for 5 minutes and then removing the solvents, the methiodide was obtained as an uncrystallisable oil (see method A). This was refluxed for 2 hours in amyl alcohol with the addition of potassium hydroxide (2 g.), and on treatment as in method A there were obtained a very small neutral fraction and a base (0·5 g.), which was identified as the original substance by the m. p.'s of its hydriodide (m. p. 176·5—178°) and perchlorate (m. p. 182—184°, not recrystallised). The decomposition of the methiodide proceeds, therefore,

as in method A, with loss of the methyl group. This unusual reaction and the m. p.'s recorded above appear to establish the identity of the bases prepared by the two methods; nevertheless, because of the failure (see p. 2568) of the perchlorate of the base prepared by method A to depress the m. p. of the perchlorate of (X), no great stress can be laid on identification of bases of this series by means of the perchlorates.

The Isomerism of the α- and β-Tetrahydrodeoxycodeines.—From a study of the literature it appeared that the important isomerism of the α- and β-tetrahydrodeoxycodeines (Knorr and Waentig, *Ber.*, 1907, **40**, 3683; Freund, Melber, and Schlesinger, *J. pr. Chem.*, 1920, **101**, 1) might be fallacious and due to the α-isomeride being a mixture of unreduced deoxycodeine and the β-tetrahydro-derivative. Nearly all the recorded properties of α-tetrahydrodeoxycodeine and its derivatives approximate very closely either to those of deoxycodeine or to those of its β-isomeride. For example, α-tetrahydrodeoxycodeine (prepared for this investigation by reduction of chlorocodide with sodium and alcohol) was purified by recrystallisation from methyl alcohol, conversion into the hydriodide, which was twice recrystallised, and crystallisation of the liberated base from methyl alcohol; it was still an ill-defined substance, sintering at 115° and melting at *ca.* 125—130°. Mixed with deoxycodeine (m. p. *ca.* 126°), it melted at *ca.* 130°. On the other hand, the *hydriodide* of the α-isomeride (not hitherto described) crystallised from water in elongated prisms, m. p. 242—243°, and that of the β-isomeride in prismatic needles, m. p. 240—241°, whilst a mixture of the two melted at 241°. On obtaining these results it was decided to test the above hypothesis, the hydrochlorides being chosen for this purpose. Deoxycodeine hydrochloride is sparingly soluble in alcohol, sinters at 165° (decomp.) and melts at *ca.* 270° (decomp.), and has $[\alpha]_D + 86°$. The hydrochloride of α-tetrahydrodeoxycodeine is also sparingly soluble in alcohol, melts at *ca.* 155° (decomp.), and has $[\alpha]_D - 17°$. The hydrochloride of the β-isomeride, however, is readily soluble in alcohol and melts at *ca.* 262°. If the above hypothesis were correct, it should be possible by fractional crystallisation of the α-salt to obtain a *dextrorotatory*, least soluble fraction and to concentrate the β-salt into the mother-liquors. Accordingly, the hydrochloride (7·5 g.) of the crude α-isomeride was fractionally crystallised from alcohol; after six crystallisations the least soluble fraction (0·8 g.) melted at 158° (decomp.) and had $[\alpha]_D^{17°} - 40°$; the base prepared from it, recrystallised from methyl alcohol, melted at 134—135° after sintering at 125°, and was lævorotatory. The liquor containing the most soluble fraction gave on evaporation a brown oil from which the base was extracted by ether after

addition of ammonia; after removal of the solvent, a red oil was obtained which could not be crystallised from methyl alcohol, although the β-base crystallises well from this solvent. As no separation had occurred and the only result of the fractionation was the preparation of α-tetrahydrodeoxycodeine in a state of slightly greater purity than hitherto, this experiment may be taken as a much-needed confirmation of the homogeneity of this base and of the reality of the isomerism. The absence of depressions noted above is remarkable, but two similar cases among closely related compounds were recorded earlier in this paper.

The author wishes to thank Professor Robinson for suggesting this research and for his continuous interest therein, and the Department of Scientific and Industrial Research for a grant which enabled him to undertake it.

THE UNIVERSITY, MANCHESTER. [*Received, July 14th*, 1926.]

CCCXXXVIII.—*New Crystalline Forms of Trimethyl Glucose and Dimethyl Glucose.*

By WALTER NORMAN HAWORTH and WILLIAM GREENWELL SEDGWICK.

THE preparation of new crystalline reference compounds in the hexose series has been undertaken with the view of assisting the constitutional investigations of the di- and poly-saccharides. Progress in the determination of the structure of the higher sugars has been impeded by imperfect knowledge of the constitution of the simplest units, and formulæ assigned to methylated hexoses during 20 years are now amended by the recognition of the amylene-oxide structure for most of the normal sugars (this vol., pp. 89, 1858).

In the series of partly methylated glucoses, two trimethyl glucoses have been recognised. These are the 2 : 3 : 6-trimethyl glucose, which is crystalline, and the 2 : 3 : 4-trimethyl glucose, which is a liquid, and each gives a crystalline glucoside. The latter appeared formerly in the literature as the 2 : 3 : 5-isomeride, but the allocation of the new ring formula to glucose introduces a corresponding amendment in the position of the third methyl group. Regarding normal glucose as an amylene oxide, one is able to deduce the possible existence of two other isomerides in the trimethyl series—the 2 : 4 : 6- and the 3 : 4 : 6-trimethyl glucoses, which have not hitherto been prepared.

Similarly, no fewer than six isomerides of dimethyl glucose may exist, of which only one has, up to the present, been isolated (Irvine and Scott, J., 1913, **103**, 575), and the structure of even this single representative is now indefinite, owing to the adoption of the amended formula for methylglucoside.

In an endeavour to explore this field completely, glucose has again been methylated with alkali and methyl sulphate under conditions selected as being favourable to the formation of partly methylated glucoses, and the first series of results is now communicated. From earlier work in this field (Haworth and Leitch, J., 1918, **113**, 194), it was known that the use of these reagents yields a preponderance of the β-glucosides. Under the procedure now described, chiefly the β-glucosides of tetramethyl glucose, trimethyl glucose, and dimethyl glucose were obtained. Separation of the various mixtures of products led to the isolation of two new crystalline varieties of trimethyl β-methylglucoside: (*a*), m. p. 67—68°, and (*b*), m. p. 64°.

The former (*a*) gave on hydrolysis a new crystalline *trimethyl glucose*, m. p. 123°, $[\alpha]$ + 89·7°, changing with acid catalysis to the equilibrium value +71·9° in water; or +110° ⟶ 69·7° in methyl alcohol. We have been unable to prepare an osazone from this sugar. The same variety of trimethyl glucose is also obtainable by an alternative method, *viz.*, hydrolysis of heptamethyl sucrose, which gives rise to a mixture of trimethyl glucoses and tetramethyl γ-fructose from which the latter can be largely removed by fractional distillation (Haworth, J., 1920, **117**, 206). The remaining liquid, which has a higher boiling point, gives rise to the trimethyl β-methylglucoside, m. p. 67—68°, already mentioned (*a*), and also to the corresponding trimethyl glucose, m. p. 123°, identical in all respects with the new sugar now described and giving in admixture with it no depression of m. p. In a previous paper, the isolation of 2 : 3 : 6-trimethyl glucose was recorded (Haworth and Mitchell, J., 1923, **123**, 310) as a product resulting from the hydrolysis of heptamethyl sucrose, and this was confirmed by two observers. The new trimethyl glucose, m. p. 123°, differs from 2 : 3 : 6-trimethyl glucose in an essential particular, in that it does not undergo inversion of sign during condensation with methyl-alcoholic hydrogen chloride at room temperature, a behaviour which is to be regarded as characteristic of the 2 : 3 : 6-variety. Although the melting point and rotation data of the two sugars are similar, the m. p. of either is depressed on admixture with the other.

We hesitate definitely to ascribe positions to the substituent groups in this crystalline trimethyl glucose, although the provisional formula suggested by the properties herein described for this sugar

is that of a 2 : 4 : 6-isomeride. We prefer, however, that the distribution of the methyl groups should be regarded as an open question for the present. The crystalline glucoside (*a*), m. p. 67—68°, may therefore be tentatively described as 2 : 4 : 6-trimethyl β-methylglucoside. The glucoside (*b*), m. p. 64°, appears to be a derivative of a different trimethyl glucose which we have not yet isolated in a crystalline form.

From the direct methylation of glucose a liquid product was obtained corresponding to a dimethyl methylglucoside. It failed to condense with acetone, but gave a crystalline derivative with benzaldehyde, m. p. *ca.* 117—119°. Hydrolysis of the glucoside yielded a pale gum which was apparently a mixture of various forms of dimethyl glucose, and from this was isolated a new crystalline *dimethyl glucose*, m. p. 156—157°, $[\alpha]_D$ +93·1° → 62·4° in water and +110° → 64·7° in methyl alcohol. That this was an amylene-oxide sugar was demonstrated by its comparative stability towards permanganate and by its ready conversion into crystalline tetramethyl glucose. The new dimethyl glucose, from which we were unable to prepare an osazone, differs widely in physical properties from the α- and β-forms of the dimethyl glucose isolated by Irvine and Scott (*loc. cit.*), who give the m. p.'s 85—87° and 108—110°, respectively.

Experimental.

Preparation of Partly Methylated Glucoses by Direct Methylation of Glucose with Methyl Sulphate.—The methylation of glucose was conducted as described by Haworth (J., 1915, **107**, 8; compare J., 1918, **113**, 188), 27—50 g. of glucose being used in one operation. Initially, the solution was maintained at 35° in the presence of an excess of methyl sulphate over the amount of alkali required, and the mixture was thus kept neutral or slightly acid until all the reducing property of the sugar had disappeared. Thereafter the temperature was raised to 70° and the methylation completed in the manner described in earlier papers, but the greatest care was exercised to avoid the development of excessive alkalinity, since this condition was harmful to the partly methylated products. After being heated at 100° for ½ hour, the solution was cooled, neutralised with dilute acetic acid, and then made faintly alkaline with sodium carbonate. Chloroform (10 c.c.) was stirred with the solution, which was then kept over-night; sodium sulphate crystallised in the interval and filtration was easy. Several extractions of the filtrate with chloroform were made and the extracts were combined with the chloroform washings of the sodium sulphate and dried. After evaporation of the solvent, the product was distilled under diminished pressure.

By varying the quantities of the methylating agent employed with 50 g. of glucose, it was found that, after one methylation using three times the theoretical quantities of methyl sulphate and alkali, 45 g. of a liquid product were obtained, but the major portion of this was the completely methylated tetramethyl β-methylglucoside. Twice the theoretical quantities for 50 g. of glucose having been used, the liquid product (37 g.) was extracted with chloroform, yielding on repeated distillation 16 g. of a fraction corresponding with tetramethyl methylglucoside, 14 g. corresponding with trimethyl methylglucoside, and 6·3 g. corresponding with dimethyl methylglucoside. When only theoretical quantities of methyl sulphate were used, a total weight of 26 g. of the methylated sugar was obtained; this was extracted with chloroform and divided into fractions of 11, 10, and 5 g.

Evaporation of the aqueous liquors to dryness gave a solid, slightly viscid mass, containing sodium sulphate, but consisting largely of sodium methyl sulphate along with partly methylated sugars. The latter were extracted with chloroform containing tetramethyl methylglucoside, the addition of which led to more complete extraction than with chloroform alone.

In view of these results, several such methylations were conducted on 50 g. of glucose, employing twice the theoretical quantities of methyl sulphate (121 c.c.) and sodium hydroxide (121 g. in 210 c.c. of water). By repeating these experiments, 150 g. of partly methylated glucose were accumulated, and submitted to six or more fractional distillations under 0·01 mm. pressure. In addition to intermediate fractions which were neglected, the material was divided into the following portions:

Fraction.	B. p.	Yield.	n_D.
I.	95°	40 g.	1·4455
II.	124—127	54 g.	1·4578
III.	146	24 g.	1·4730

The following constants of these fractions varied only slightly in different preparations, and constitute a trustworthy average based on several results.

Fraction I. Colourless liquid, $[\alpha]_D$ +72° in water ($c = 2$) [Found: OMe, 61·1. Calc. for $C_6H_7O(OMe)_5$: OMe, 62·0%]. Hydrolysis yielded the characteristic crystalline tetramethyl glucose, m. p. 86—87°, $[\alpha]_D$ in water +90° → +84·1°.

Fraction II. Colourless liquid, which failed to crystallise on nucleation with a crystal of 2 : 3 : 4-trimethyl β-methylglucoside; $[\alpha]_D$ +4° in water ($c = 2·8$) [Found: OMe, 50·6. Calc. for $C_6H_8O_2(OMe)_4$: OMe, 52·5%]. This corresponded with a trimethyl β-methylglucoside. It was unaffected by 0·25% hydrochloric acid

at 100°, but with 5% acid hydrolysis was complete in 3½ hours, the specific rotation being constant at +68°. This specimen was submitted to further methylation with Purdie's reagents, yielding tetramethyl methylglucoside, which hydrolysed to give crystalline tetramethyl glucose.

Fraction III was a colourless, viscid liquid, sparingly soluble in ether and benzene, $[\alpha]_D$ +1·0° in water ($c = 5·9$). On repeated fractionation this value changed to $[\alpha]_D$ +12° [Found : OMe, 41·5. Calc. for $C_6H_9O_3(OMe)_3$: OMe, 41·9%]. By hydrolysis with 3% hydrochloric acid at 100°, a constant value +62·4° was attained after 5 hours. Complete methylation of this fraction, followed by hydrolysis of the tetramethyl methylglucoside, yielded crystalline tetramethyl glucose.

Isolation of Trimethyl Glucoses.—Hydrolysis of fraction II with 5% hydrochloric acid at 100° gave the following polarimetric readings : $[\alpha]_D$ (initial) +4° ; +16° (after 20 mins.) ; +30° (40 mins.) ; +41° (60 mins.) ; +59° (120 mins.) ; +65° (180 mins.) ; +66° (200 mins.). With a portion of the material of fraction II, hydrolysis was carried out with 8·8% hydrochloric acid during 2 hours. The product was a pale yellow syrup, n_D 1·4735, gradually depositing colourless needles which were separated. Distillation of the major portion of the sugar (b. p. 145—148°/0·04 mm.) yielded a colourless liquid which was collected in three portions. The middle fraction (n_D 1·4740) partly crystallised over-night, and addition of dry ether promoted further crystallisation. Two crystallisations from ether gave a constant m. p. of 123°. The colourless needles showed $[\alpha]_D$ in methyl alcohol ($c = 1·77$) +110° ⟶ 69·7° ; in water ($c = 2·0$) +89·7° ⟶ 71·9°. In methyl alcohol containing 0·25% of hydrogen chloride at room temperature the sugar showed no inversion of rotation : $[\alpha]_D$ (initial) +78° ; +71° (after 1 hr.) ; +70° (5 hrs.) ; +69° (12 hrs.) ; +69° (7 days) ; +68° (45 days). Thereafter this solution was heated at 40° for a further period of 5 days ; it was then almost devoid of action towards Fehling's solution. At this stage the solution was neutralised with silver carbonate, the methyl alcohol distilled, and the product extracted with ether. Removal of the ether left a syrup which rapidly crystallised, and after being kept for 2 days on porous tile the colourless needles were washed several times with light petroleum and then melted at 67°. This compound was identical with another specimen prepared from a crystalline trimethyl glucose obtained by hydrolysis of heptamethyl sucrose. Two specimens of trimethyl methylglucoside showed $[\alpha]_D$ −12·3° in water ($c = 0·5$).

A further portion of fraction II (20 g.) was submitted to repeated fractional distillation and the products were collected in six portions,

the first of which distilled at 123°/0·01 mm., and the last at 128°/0·01 mm. The first five portions crystallised on nucleation with a specimen of the trimethyl methylglucoside obtained above, but the third fraction, b. p. 126°, n_D 1·4575, crystallised completely and these crystals were examined after being washed with light petroleum: large fine needles, m. p. 67—68°, $[\alpha]_D$ −19·1° in water (c = 2·25); −13·5° in methyl alcohol (c = 0·77) [Found: C, 50·8; H, 8·5; OMe, 51·1. Calc. for $C_6H_8O_2(OMe)_4$: C, 50·85; H, 8·5; OMe, 52·5%]. The glucoside was readily soluble in all organic solvents, but no crystallising medium was found. Hydrolysis was effected at 100° with 5% hydrochloric acid during 4 hours. The following rotation values were observed during the course of the hydrolysis: $[\alpha]_D$ (initial) −17·1°; +7·4° (after 30 mins.); +30° (60 mins.); +46·8° (90 mins.); +56·5° (120 mins.); +70° (180 mins.); +71·3° (240 mins.). The product derived from this hydrolysis was isolated by the usual methods, and the syrup, dried at 60°/15 mm., immediately crystallised. On recrystallisation from dry ether, colourless needles were obtained, m. p. 123°, showing no depression of m. p. with the specimen of the trimethyl glucose obtained as described above.

The fractions (4) and (5) in the previous fractionation of the glucoside had partly crystallised, and the crystals were separated on porous tile, washed with light petroleum, and then melted at 50° with softening at 30°. Further washing with light petroleum did not affect the m. p. and the crystals were evidently the methylglucoside (Found: C, 50·8; H, 8·5%); $[\alpha]_D$ −21° in water (c = 1·0). By mechanical means the mixed crystals were separated into two portions, and from one of these, after repeated washing with light petroleum, a small quantity was obtained, m. p. 64°. When this was mixed with the specimen of trimethyl methylglucoside already described as melting at 67—68°, the m. p. was depressed to 35—50°. In admixture with a specimen of 2 : 3 : 4-trimethyl β-methylglucoside, m. p. 92°, a m. p. 48—52° was recorded. Hydrolysis of the original mixture of crystals was carried out in the usual way, yielding a syrup which partly crystallised. The crystals were identical with those of the trimethyl glucose described above, m. p. 123°.

Dimethyl Glucose.—The fraction III obtained on distillation (p. 2577) showed $[\alpha]_D$ +1·1° in water (c = 5·0), but after repeated distillation a value of +12·2° was obtained. In a preliminary experiment an attempt was made to condense this glucoside with dry acetone containing a trace of hydrogen chloride, but, as no alteration of rotation occurred during 24 hours, it appeared that little, if any, condensation had occurred. Hydrolysis of the dimethyl methylglucoside was conducted with 3% hydrochloric acid at 100°:

$[\alpha]_D$ (initial) +1·0°; +19·1° (after 30 mins.); 30·3° (1 hr.); 47·1° (2 hrs.); 54·0° (3 hrs.); 59·1° (4 hrs.); 60·0° (5 hrs.). Hydrolysis then appeared to be complete, but for the isolation of the corresponding sugar in quantity the hydrolysis was conducted with 10% hydrochloric acid for 30 minutes in a boiling water-bath, the specific rotation then increasing from +1·0° to +62·6°. After neutralisation of the mineral acid, evaporation, and extraction of the sugar with dry acetone, a viscid gum remained, $n_D^{20°}$ 1·4867, which is hereinafter referred to as specimen (A). After 12 hours' drying at 60° in a vacuum, crystallisation occurred, and when the syrup was maintained at 40° for a week a semi-solid mass was obtained. The adhering syrup was removed by extraction with cold ethyl acetate and the remaining crystals were purified also from this solvent, giving prismatic needles, m. p. 156—157°.

This crystalline specimen of a dimethyl glucose reduced Fehling's solution on warming to 90°, but did not reduce cold neutral permanganate. It showed $[\alpha]_D$ in methyl alcohol ($c = 0·8$) +110·7° → 64·7° (after catalysis); in water ($c = 0·5$), 93·1° → 62·4° [Found: C, 46·0; H, 7·9; OMe, 28·2. $C_6H_{10}O_4(OMe)_2$ requires C, 46·15; H, 7·7; OMe, 29·8%].

The new crystalline dimethyl glucose was methylated several times with Purdie's reagents, and on hydrolysis of the distilled product, crystalline tetramethyl glucose was isolated, m. p. 84°, giving no depression in admixture with an authentic specimen of the latter sugar.

The unchanged portion of the dimethyl glucose which, as indicated above, was removed from the crystals with ethyl acetate, was placed in contact with methyl alcohol containing 0·25% hydrogen chloride. A change in specific rotation occurred after 9 days at room temperature from +64·3° to +27·1°, and after 45 days condensation appeared to be complete. The mixture of glucosides isolated showed n_D 1·4737. A portion of this liquid product was heated with methyl alcohol containing 0·5% of hydrogen chloride at 110°, and the specific rotation increased from +27° to +82°. This change evidently represented interconversion of the glucosides, and, in view of the subsequent details, represented also a structural change from the γ-glucoside to the more stable form of α- and β-isomerides. The remaining major portion of the mixture of dimethyl methylglucosides was subjected to partial hydrolysis by digestion for 2 hours at 100° with 0·4% hydrochloric acid. After neutralisation and isolation of the products in the usual way, any unchanged glucoside was extracted with small quantities of dry benzene, and was obtained as a viscid liquid, b. p. 155°/0·05 mm., $[\alpha]_D$ +57·9° in water ($c = 0·81$) (Found: OMe, 40·1. Calc.: 41·9%).

A further specimen of the liquid dimethyl glucose (A) was dissolved in dry methyl alcohol containing 0·25% of hydrogen chloride and maintained at 20° for 10 days ($[\alpha]_D$ +27°), and the syrup isolated (n_D 1·4782) was repeatedly extracted with benzene.

The extract was distilled, b. p. 140—144°/0·01 mm., and gave a colourless liquid, n_D 1·4710, which instantly decolorised neutral permanganate but was devoid of action on Fehling's solution. It showed $[\alpha]_D$ −7·9° (c = 1·4) [Found: C, 48·4; H, 8·2; OMe, 43·0. $C_6H_9O_3(OMe)_3$ requires C, 48·6; H, 8·1; OMe, 41·9%]. Hydrolysis with 0·4% hydrochloric acid at 90° gave a syrup, n_D 1·4820, which gave analyses for a dimethyl glucose (Found: OMe, 30·1%).

A portion of this dimethyl γ-methylglucoside was subjected to complete methylation with methyl iodide and silver oxide, and the resulting tetramethyl methylglucoside was isolated as a mobile liquid, n_D 1·4440, which decolorised permanganate, but had no effect on Fehling's solution. It showed $[\alpha]_D$ −3·2° in water (c = 0·95) (Found: OMe, 60·0. Calc.: 62·0%). Hydrolysis of this glucoside, which appeared to be identical with tetramethyl γ-methylglucoside, was conducted with 0·4% hydrochloric acid for 2 hours at 100°, the specific rotation changing from −3·2° to −6°. The corresponding sugar was isolated in the usual way, and this showed n_D 1·4523, $[\alpha]_D$ −6·1° in water (c = 1·0) (Found: OMe, 52·6. Calc.: 52·5%). The constants are similar to those recorded for tetramethyl γ-glucose, and the sugar decolorised permanganate and reduced Fehling's solution actively.

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[*Received, July 31st,* 1926.]

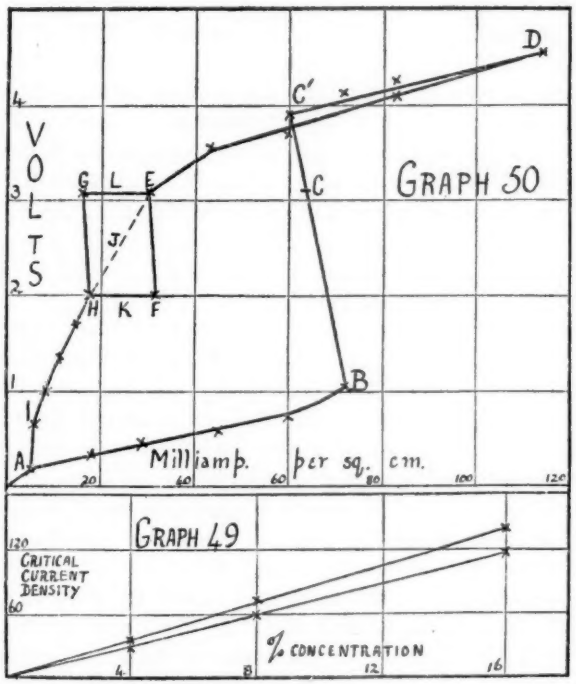
CCCXXXIX.—*Periodic Phenomena at Anodes of Magnesium, Zinc, Cadmium, Mercury, Tin, and Lead, and at an Unattackable Anode.*

By ERNEST SYDNEY HEDGES.

A RECENT paper (this vol., p. 1533) described the course of the electrolysis of a number of solutions with anodes of copper and of silver at varying current densities. It was shown that the electrode in many cases existed in one state at low current densities and in another state (covered with a poorly conducting film) at high current densities, whilst there existed a well-defined intermediate region in which the electrode alternated in regular periods between these two states. The present investigation is an extension of this work to other metallic electrodes.

One point of difference may be noticed between these experiments and those formerly described. Whereas in the experiments with copper and silver the region of periodicity could be reached by progressively increasing the current density, that is not always the case with the present series of metals. Instead, the electrode is first made to assume its pseudo-passive state by employing a high current density, and then the current is reduced until the region of periodicity is encountered.

FIG. 1.



EXPERIMENTAL.

The experimental method was described in the former paper (*loc. cit.*). The experiments were conducted at 30°, and the solutions were stirred by a stream of air bubbles. A platinum cathode was used throughout.

(1) *Zinc Anode.*

Sodium Hydroxide Solutions.—At low current densities a zinc anode dissolves in sodium hydroxide solution with formation of sodium zincate. At higher current densities a film forms over the metal, the *P.D.* rises, and oxygen is evolved, but at the same time

the zinc continues to dissolve. By suitably reducing the current, a region of oscillating potential is encountered.

The Current Density–Potential Curve.—Graph 50 (Fig. 1) shows the *P.D.* between the zinc anode and the platinum cathode in electrolysing an 8% solution of sodium hydroxide with increasing current density. For low values of current density, the *P.D.* rises along the line AB until the critical value 72 milliamp./sq. cm. is reached. At this point a film forms over the electrode and the *P.D.* rises from 1·1 to 3·1 volts (C). After the lapse of a second or so, evolution of oxygen ensues and the *P.D.* rises to 3·9 volts (C′). Further increase in current density causes the *P.D.* to rise slowly along the line C′D. If the current is now gradually reduced, the *P.D.* retraces approximately the same path and continues to the point E. If an attempt is made further to reduce the *P.D.* along EJH, it falls of its own accord to a considerably lower value and then regains the value 3·0 volts by a series of *damped* oscillations, *i.e.*, the *P.D.* oscillates with damping between E and F, L and K, G and H, etc. The point H represents the lower limiting current density for periodicity, and on further reduction the *P.D.* falls along HI and at the point I decreases rapidly.

The Nature of the Damped and Continuous Periods.—In order to realise the conditions for periodicity in this system, a current density somewhat greater than 72 milliamp./sq. cm. should be used, and after the film has formed and the *P.D.* has assumed the high value, it should be reduced slowly to 3·0 volts and then quickly to any value between 2 and 3 volts. Examples of the damped curves are given in Graph 46 (Fig. 2), where A shows the rapid damping when the *P.D.* is reduced to 2·9 volts, B represents a reduction to 2·8 volts, C shows the effect of reducing the *P.D.* to 2·7 volts, and D records well-developed oscillations obtained by reducing it to 2·3 volts. In general, the further the *P.D.* is reduced in the direction of H (Graph 50) the slower is the damping of the oscillations, whilst systems represented between E and J are rapidly damped. The longer series are preceded by an induction period (not plotted in Graph 46D).

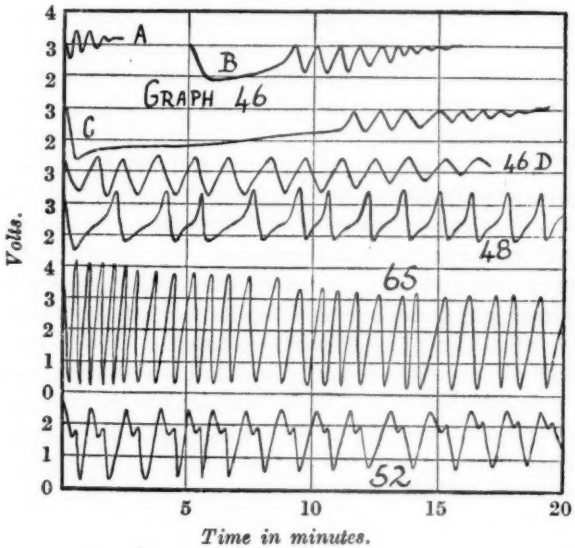
In 16% sodium hydroxide solution the same series of events occurs, but the oscillations taking place within the corresponding region of periodicity are continuous instead of damped. They may continue for many hours. The difference is doubtless due to the superior solubility of zinc oxide in the stronger alkaline solution. The limits between which the periods are to be observed are also much wider. An example of these continuous waves is given by Graph 48 (Fig. 2). These periods were investigated at 20—80°; with rising temperature the critical current density required to

produce the film and the frequency of the periods both increased. In 4% sodium hydroxide solution, damped periods were obtained, but their region of existence was very narrow.

Graph 49 (Fig. 1) shows that the critical current density required to produce the film, the final current density after formation of the film, and the potential of oxygen evolution are all linear functions of the concentration of the solution between the values 4% and 16%

At the critical current density, a white film, probably of zinc hydroxide, travels up the metal and the *P.D.* rises. Almost

FIG. 2.



immediately the film turns brown, oxygen is evolved, and the *P.D.* rises still further. Eventually the film becomes black. This film was observed by Newbery (J., 1916, **109**, 1073), who promised an investigation of its nature. It may be simply zinc oxide, for it is readily soluble in acids and alkalis, and zinc oxide is known to pass into a brown form under the influence of compression, light, etc. (Tafel, *Ann. Physik*, 1903, **11**, 613).

The production of periods depends on reducing the *P.D.* to just below the point of incipient oxygen evolution. The line GLE is almost equipotential with C (Graph 50). In 8% solutions, the film remains on the anode throughout the periods and oxygen is evolved just at the peaks of the waves. In 16% solutions, at the peaks of the waves where evolution of oxygen occurs, the film is thrown off into the solution and a fresh film forms at the lower value of poten-

tial. The electrode only preserves its metallic surface below the point represented by I, where a sudden drop in the *P.D.* occurs. The oscillation, then, is not between the states represented by AB and C′D, as in the experiments with copper, but is, in this case, between the states BC and CC′. This explains why the periods are obtained by reduction from a high voltage rather than by progressive increase in current density. The periods are formed by carefully setting the system in the state represented by point C, where it has equal opportunities of existing in the state CC′ or CB; but the point C cannot be reached from below, for the film sets in at B and the *P.D.* rises rapidly.

Sulphuric Acid Solutions.—Solutions of the following concentrations * were examined: 100, 90, 60, 50, 45, 42, 40, 35, 30, 5, 2, 1, 0·5, 0·1%. The 100% and 90% solutions were almost non-conducting, owing to the formation of an insoluble film of zinc sulphate. In the 60% and 50% solutions, the sulphate film readily formed over the electrode, the *P.D.* rising to a high value and oxygen being evolved. With solutions below 35%, the preliminary reaction of the zinc with the acid was very energetic and no film formed on the electrode over the range of current densities employed. In the case of the very dilute solutions (below 2%), an oxide film formed on the electrode at high current densities, but this was loosely adherent and did not appreciably affect the strength of the current.

The range of concentrations favourable to periodic phenomena is 40—45% of sulphuric acid, which is intermediate between the regions of permanent existence and of non-existence of the sulphate film: the best concentration is 42%—in this solution, at a current density of 142 milliamp./sq. cm., a white film sweeps up the metal and the *P.D.* rises to 3·3 volts. The *P.D.* should then be reduced to below 2·5 volts. As in the sodium hydroxide solutions, in this case also the *P.D.* drops of its own accord some way farther still and then periodically regains the value 2·5 volts, which is the potential of oxygen evolution in this solution. An example of the continuous periods produced, showing an amplitude of 2 volts, is given in Graph 52 (Fig. 2). A visible sign of the periodicity is the evolution of oxygen every time the *P.D.* reaches its highest value. Reduction of the *P.D.* to different values showed that the frequency increases at lower current densities.

Since the phenomenon is produced under conditions such that the zinc sulphate film is given opportunities both of being formed and of dissolving, it was hoped to obtain similar effects in strong aqueous

* Throughout this paper "% concentration of acid" means the number of c.c. of sulphuric acid (*d* 1·84), nitric acid (*d* 1·42), or hydrochloric acid (*d* 1·16) per 100 c.c. of solution.

solutions of zinc sulphate. These were not realised, however, for all changes were exceedingly sluggish, perhaps as a result of the high viscosity of the liquid. A solution saturated at 30° with $ZnSO_4,7H_2O$ took a current of 20 milliamp./sq. cm. before the formation of a film. This indicated that such a solution can dissolve considerably more anhydrous zinc sulphate. When the film formed, the *P.D.* rose from 0·8 volt to 4·6 volts in the course of several minutes, and then oxygen was evolved. Periods could not be obtained on reducing the *P.D.*, every movement of the voltmeter needle taking several minutes for its completion. Similar unsuccessful attempts were made with solutions 90% and 80% saturated.

Experiments in Other Solutions.—The following is a list of solutions in which periodic phenomena were not encountered, together with brief notes on their behaviour: Hydrochloric acid, 10, 5, 2, 1, 0·5% : at very high current densities a dark grey film formed on the metal, but did not affect the current strength; nitric acid, 20, 12·5, 10, 5, 2·5, 1, 0·5% : at high current densities, a non-adherent, white, flaky substance fell continuously from the anode; potassium cyanide, 20, 10, 5, 2·5% : these solutions behaved as if they were dilute potassium hydroxide solutions; ammonium chloride, 5, 2%; ammonium sulphate, 10, 5, 2, 1%; sodium nitrate, 5% : loose gelatinous zinc hydroxide fell continuously from the anode even at fairly low current densities; potassium iodide, 3%; potassium chromate, 10%; sodium phosphate, 5% : insoluble films readily formed over the anode; sodium hydrogen sulphite, 4, 2%; sodium acetate, 7·2%; acetic acid, 6%.

(1A) *Zinc Amalgam Electrode.*

Periods similar to those described for zinc were obtained with an amalgamated zinc electrode in 42% and 30% solutions of sulphuric acid. In the former case, a white film formed over the anode at a current density of 50 milliamp./sq. cm. and the *P.D.* rose to 11·5 volts. On reducing it to 2·6 volts, continuous oscillations between 2·6 and 0·8 volts ensued. These had a period of 30 seconds.

With this system, although the method of procedure outlined above is the readiest means of producing the effect, the periods enter without any adjustment of the potential if a slightly lower current density than that advised is employed and the electrolysis is allowed to proceed for an hour or so. Joule (*Phil. Mag.*, 1844, **24**, 106) noticed periodic film formation in this system.

(2) *Cadmium Anode.*

Sodium Hydroxide Solutions.—Cadmium oxide, unlike zinc oxide, is not soluble in sodium hydroxide solution, and periodic film

formation is therefore not to be expected. A brown film formed over the anode and oxygen was evolved at quite low current densities. Since the oxide is soluble in ammoniacal solutions, however, an attempt was made, but unsuccessfully, to produce periodic phenomena by electrolysing various mixtures of sodium hydroxide and ammonia.

Sulphuric Acid Solutions.—The following concentrations were examined over the range of current densities available: 100, 80, 60, 40, 35, 30, 25, 20, 10, 5, 2, 1%. In solutions of 60% and above, an insoluble sulphate film readily formed over the electrode, and no film formed at the current densities used in solutions weaker than 20%. The concentration range of existence of periodic phenomena is 25—35% of sulphuric acid. Since the best effect is obtained in 30% acid, the conditions will be described for that concentration. The concentration range is below that of zinc.*

In 30% sulphuric acid solution, a white film formed over the cadmium when the current density was raised to 108 milliamp./sq. cm. and the *P.D.* rose from 0·3 volt to 12·0 volts, oxygen being evolved. The *P.D.* was then reduced to 4·0 volts and continuous periods of large amplitude followed. An example in which the *P.D.* oscillated between 0 and 3—4 volts is given in Graph 65 (Fig. 2). At the peaks of the waves evolution of oxygen occurred.

Potassium Cyanide Solutions.—Oscillations between 2·6 and 3·0 volts were obtained in 5% potassium cyanide solutions by using a current density of 42 milliamp./sq. cm. and, after formation of the film, reducing the *P.D.* to 3·0 volts. The cadmium then dissolved as the double cyanide. In a 2·5% solution, periods from 2·2—2·4 volts were obtained similarly. Periods were not produced in 10% and 20% solutions.

Experiments in Other Solutions.—The following did not furnish periodic phenomena: Hydrochloric acid, 10, 5, 2, 1%; nitric acid, 10, 5, 2, 1%; in the more dilute solutions a white, flaky substance fell continuously from the anode at somewhat elevated current densities; ammonium sulphate, 10, 5, 1%.

(3) *Mercury Anode.*

The mercury used in these experiments was redistilled immediately before use. It was contained in a small glass cup 1 cm. in diameter, of the type used in the ordinary mercury voltameter. A

* The following incident testifies to the reproducibility of these results. The author was given a sheet of metal reputed to be cadmium; its behaviour in various solutions was investigated and the limits of periodic action were determined. The results obtained were identical with those for zinc, and it was then found that the metal was in reality zinc.

special feature of the mercury periods is that a concomitant periodic change in the surface tension occurs, causing the mercury surface alternately to be flattened and elevated.

Potassium Cyanide Solutions.—These experiments were conducted at 20° and the solutions were not stirred. The mercury surface remained bright until the current density reached 70 milliamp./sq. cm. At this point a black film spread over the surface, causing the meniscus to flatten, and the *P.D.* rose from 2·3 to 4·0 volts, oxygen being evolved. The periods were best produced by then lowering the *P.D.* to 3·0 volts. This gave a continuous oscillation in 10-second periods between 2·6 and 2·9 volts. On slightly increasing the current density the oscillation was between 2·8 and 3·3 volts and, in accordance with the general rule, the frequency was lower at the higher current density. The film remained throughout, but a few bubbles of oxygen were evolved at the crests of the waves. The mercury meniscus flattened perceptibly while the potential was at the lower value and became more convex at the higher value.

The periods may also be formed directly by electrolysing the solution with a *P.D.* of 2·0 volts; the black film will then form in 15 minutes or so and will be followed by the oscillations. The formation of the film is generally preceded by much trembling on the part of the mercury surface and the voltmeter needle. The upper limit of the region of periodicity is 3·5 volts. Similar periods of lower frequency were obtained in 10% potassium cyanide solution. The reaction is probably similar to the experiments with copper—hydroxyl ions are discharged first and the mercurous oxide dissolves in the potassium cyanide.

Sodium Hydrosulphide Solutions.—In a 10% solution a black film readily formed over the anode. Periods similar to those obtained in potassium cyanide solution were produced by applying a current density of 7 milliamp./sq. cm. These were between 1·0 and 1·2 volts.

Nitric Acid Solutions.—The concentrations examined were 40, 25, 10, 5%. In the last two solutions, a yellow, basic mercurous nitrate formed at a certain critical current density. In the 40% solution, a grey, crystalline film, probably of mercurous nitrate, formed at high current densities. In the 25% acid at a current density of 20 milliamp./sq. cm., a grey film formed and the mercury surface pulsated rapidly and continuously, although the voltmeter needle remained constant at 1·1 volts. After a time, the *P.D.* rose suddenly to 3·2 volts, the film became thick and white, and the pulsations ceased. On reducing the current very slightly, the *P.D.* dropped again to 1·1 volts and the rapid pulsations (3 or 4 per second) continued. Occasionally the pulsations did not affect the

mercury meniscus as a whole, but took the form of gyrations starting from some point on the periphery.

Experiments in Other Solutions.—Periodicity was not encountered in the following solutions: Hydrochloric acid, 25%: insoluble mercurous chloride formed on the anode at the lowest current densities; sulphuric acid, 100, 20, 10, 5, 2, 1%: insoluble mercurous sulphate formed; sodium hydroxide, 8%: at the lowest current densities an insoluble, yellow film formed on the electrode and oxygen was evolved. Potassium iodide solutions (40, 30, 20%) were expected to yield periodic phenomena, since the film formed dissolved in the solution when the circuit was broken. All attempts to render the system periodic by increasing the solvent power of the potassium iodide (employing strong solutions and extending the examination up to 60°) were fruitless. When mercurous iodide dissolves in potassium iodide, however, it goes into the mercuric state, with separation of mercury. It seems possible that this complication stops the periodicity.

(4) *Magnesium Anode.*

Only one example, and that a poor one, of periodicity at a magnesium anode has been found.

Sulphuric Acid Solutions.—The following concentrations were examined: 100, 95, 90, 80, 75, 70, 65, 60, 55, 50, 45, 40%. The behaviour was not quite the same as in the corresponding experiments with zinc and cadmium. In solutions of concentration 70% and above, a resistant film very readily formed on the anode and the *P.D.* rose to a high value; the metal, however, then assumed a peculiarly bright lustre. On breaking the current, the high potential state persisted. This is not unlike the passivity phenomenon observed with anodes of iron and nickel. The metal continues to dissolve when in this state. In solutions weaker than 50%, magnesium dissolved with great vigour and the surface remained dull. Only at the concentration 65% was any periodic effect observed. With a current density of 50 milliamp./sq. cm., the *P.D.* rose suddenly to 5·0 volts. On reducing it slowly to 1·8 volts, slow oscillations between 1·2 and 1·5 volts followed.

In this group of elements, therefore, the limits of periodicity in sulphuric acid solution are defined by the following concentrations: Magnesium, 65%; zinc, 45—40%; cadmium, 35—25%; mercury, nil.

Experiments in Other Solutions.—All these failed to give periodic effects: Hydrochloric acid, 3%; sodium hydroxide, 8%; ammonium chloride, 1%; ammonium sulphate, 5, 0·5%; potassium iodide, 2%; potassium cyanide, 10, 5, 2, 1%; sodium nitrate, 2%; sodium phosphate, 5%.

(5) *Tin Anode.*

Sulphuric Acid Solutions.—100, 90, 60, 40, 30, 20, 10, 5, 3, 1, and 0·5% Solutions were examined. The phenomena observed were in every respect similar to those with zinc and cadmium electrodes. Periods were produced only in the 5% solution. With a current density of 175 milliamp./sq. cm. a white film formed over the anode, the potential rising from 1·7 to 4·4 volts. After the lapse of a second or so, evolution of oxygen set in and the potential rose further to 5·7 volts. Reduction to 4·0 volts gave a damping oscillation. Reduction to 3·0 volts proved to be too low, for the film came off entirely. By reducing the potential to 3·5 volts, continuous oscillations between 2·2 and 3·2 volts followed, having a period of one minute.

Nitric Acid Solutions.—100, 80, 60, 40, 30, 20, 10, 5, 2, 1, and 0·5% Solutions were examined. In those stronger than 40% the preliminary reaction was extremely vigorous, giving a voluminous product of hydrated stannic oxide. In 100% nitric acid, once the reaction had started, it required a current density of roughly 10,000 milliamp./sq. cm. to form a coherent film of oxide, which stopped further action even when the circuit was broken. In solutions below 20%, a grey substance (probably a mixture of stannic and stannous oxides) fell continuously from the anode. Periodic phenomena occurred in 1% and 0·5% solutions. In the former case, a black film formed over the anode at a current density of 30 milliamp./sq. cm. and the *P.D.* rose from 1·1 to 1·6 volts. By reducing it to 1·3 volts, continuous oscillations between 1·1 and 1·5 volts followed.

Experiments in Other Solutions.—No periodic phenomena observed: Hydrochloric acid, 30, 15, 10, 5, 2, 1%: in the last two solutions a dark film of stannous oxide formed slowly at high current densities, but did not appreciably impede the current; potassium cyanide, 20, 10%: the solution behaved as though it were dilute potassium hydroxide; ammonium chloride, 10, 2%; sodium nitrate, 10, 5%: these solutions soon became cloudy with a white, gelatinous precipitate, part of which loosely adhered to the anode. With sodium hydroxide (32%), there should be a possibility of periodicity. A film formed on the anode at a certain critical current density, but on breaking the circuit the film was very slow to dissolve. Experiments were then carried out at various temperatures up to 80° in an attempt to quicken the dissolution of the film, but the movements of the voltmeter needle were still very sluggish.

(6) *Lead Anode.*

The experiments with lead have furnished only one case of a periodic effect. In fact, the behaviour of lead as an anode is truly

saturnine, all changes in potential being exceedingly sluggish and sometimes taking 10 minutes for completion. In general, periodic phenomena seem to be best developed in a film which forms rapidly over the electrode, whilst experience goes to show that a slowly-forming film does not exhibit periodic phenomena. If the periodicity is in all these cases connected with a certain instability of the film as first deposited (this point having been demonstrated at least in the case of copper), it may be that a slowly forming film assumes a stable state before its completion.

Sodium Hydroxide Solutions.—At low current densities, the lead anode dissolved smoothly and at a certain value a film of lead peroxide formed over the metal, the *P.D.* rose, and oxygen was evolved. Solutions of composition 32, 16, 8, 4, 1% were examined at 20—60°. The formation of the film was very slow and only at the higher temperatures and concentrations did the film redissolve when the circuit was broken. Continuous periods were never realised, but in a 32% solution at temperatures above 50° the rise in *P.D.* denoting film formation was always preceded by several preliminary oscillations. It appears that the film may exhibit periodicity when incompletely formed, but not after it has entirely covered the electrode.

Negative Results with Lead.—In the following solutions, changes in potential were exceedingly sluggish and periodicity was not observed: Hydrochloric acid, 100, 60, 40, 25, 10, 5, 2, 0·5% at 30—90°; sulphuric acid, 100, 50, 20, 5%; nitric acid, 30, 20, 10, 5, 2, 1%; potassium cyanide, 10, 2·5%; ammonium acetate, 10, 1%; potassium iodide, 3%.

Discussion.

The present work and the previous experiments on copper and silver embody the results of the examination of more than 500 different systems, and from this exhaustive study it is possible to lay down some of the conditions necessary to secure periodic effects. (1) A film must form over the anode. (2) This film must be soluble in the electrolyte when the circuit is broken. It follows that the electrode may exist in one of two possible states—with or without the film. This leads to the third condition. (3) The current density must be between two well-defined limits which depend on the temperature, concentration, and nature of the solution. Periodic phenomena can be realised by so arranging the current density that the electrode has almost equal chances of remaining in one state or passing into the other. The result is that the electrode oscillates continuously between these two states. The region over which this periodic effect can be observed is often very narrow, but some-

times (as in the case of copper in hydrochloric acid) is quite extensive.

The results which have been described illustrate very forcibly the conditions which have just been laid down. Some other factor is required, however, in order to explain the fundamental *cause* of the periodicity. Although in one case it has been shown that the film first appears in a metastable form, there is not yet sufficient evidence to regard this as a general explanation. It is hoped that further evidence on this point will result from the experiments at present in progress.

(7) *Platinum Anode.*

In order to test the conclusions set forth in the Discussion from a different point of view, experiments were carried out on film formation at an unattackable anode of platinum.

If a film is deposited electrolytically on the anode under such conditions that it will redissolve in the electrolyte when the circuit is broken, periodic film formation should occur when the current density is such that the rates of formation and dissolution of the film are approximately equal.

To devise favourable cases for such a study at the anode was a matter of some difficulty. The most suitable case would be the electrodeposition of sulphur from solutions of alkali sulphides and of iodine from alkali iodides. The former case was examined by Köhlichen (*Z. Elektrochem.*, 1901, **7**, 629) and by Küster (*Z. anorg. Chem.*, 1905, **46**, 113), and well-defined regular periods were observed under certain conditions. Similar periods were observed by Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1291) in the electrolysis of solutions of iodides. Although the cause of this effect was not apparent at the time, it seems that the periodicity was observed between certain limits such that the film had approximately equal chances of forming and of dissolving. The fact that ease of periodic film formation was parallel with facility of polyiodide formation is additional evidence on this point.

Windelschmidt (*Diss.*, Münster, 1907) and Dietrich (*Diss.*, Münster, 1910) examined the anodic deposition of nickel hydroxide from ammoniacal solutions of nickel sulphate and found that under certain conditions a film of nickel hydroxide alternately formed and dissolved in the ammonia.

The author has studied the electrolysis of a number of solutions of this type and has observed periodicity in several cases. In many instances, however, the films are poorly adherent and the resulting waves are very irregular, whilst in others the films are so loose that the current strength is not affected thereby. No attempt has been made to fix the best conditions for the appearance of periodic

phenomena in these systems, the sole object of the examination being to test the views expressed above on periodic anodic phenomena.

Ammoniacal Silver Nitrate Solutions.—Solutions of silver nitrate containing a considerable excess of ammonia deposited all the silver on the cathode. Solutions which were precipitated by ammonia, the precipitate being incompletely redissolved, after filtration deposited silver on the cathode and black silver peroxide on the anode. By using a little more ammonia the silver peroxide was given an opportunity to redissolve, and then periodic phenomena were realised between certain limiting current densities. A typical solution consisted of 50 c.c. of $N/10$-silver nitrate, and 10 c.c. of $2N$-ammonia made up to 100 c.c., and was electrolysed at 30° with a current density of 40 milliamp./sq. cm. The *P.D.* oscillated between 2·4 and 2·7 volts in periods of 1·5 minutes. The frequency decreased with increasing current density. Several other solutions of varying composition were tried with equal success, but no systematic examination of the effect of varying the conditions was attempted.

Incidentally, although silver peroxide is produced at the anode when strong solutions of silver nitrate are electrolysed, it is curious that it should be obtained in the ammoniacal solutions described above, where all the silver is supposed to exist as the $Ag(NH_3)_2^{\cdot}$ ion. This point might repay investigation, for the effect is not produced if ammonia is added in excess.

Potassium Silver Cyanide Solutions.—When an excess of potassium cyanide was used, the only product was silver at the cathode. Filtered solutions containing insufficient potassium cyanide to redissolve all the precipitated silver cyanide gave, in addition to silver at the cathode, a deposit of silver cyanide on the anode. By adding a very slight excess of potassium cyanide irregular periods were produced. The lack of regularity is probably to be traced to the " patchy " nature of the film.

Copper Solutions.—Solutions of cupric chloride or cupric sulphate containing just sufficient ammonia to redissolve the precipitated hydroxide gave different products at the anode, according to the current density used. To 50 c.c. of 5% cupric chloride was added the required amount of ammonia and the solution was then made up to 100 c.c. In addition to a deposit of metallic copper on the cathode, at a current density of 4 milliamp./sq. cm., a black deposit of cupric oxide formed on the anode : at a current density of 8 milliamp./sq. cm., the anodic product was blue cupric hydroxide, whilst at current densities above 40 milliamp./sq. cm. no film formed and oxygen was evolved.

In the presence of a slight excess of ammonia feeble periods were

observed in the onset of the first cupric oxide film. On addition of more ammonia the only anodic product was oxygen. At low current densities the cupric oxide was deposited on the platinum anode initially in a film so thin as to give a series of bright interference colours resembling those to be seen on the surface of copper (compare Evans, J., 1925, **127**, 2487).

Solutions of copper salts were precipitated by potassium cyanide and the precipitate was just redissolved. The results of electrolysis were similar to those in the case of ammoniacal solutions in that at low current densities a golden-brown cyanide film formed on the anode, whilst on slightly increasing the current density the product was a green basic cyanide and at higher current densities only oxygen was produced. In these solutions, however, periodicity was never observed.

Electrolysis of Other Solutions.—Feeble periods were encountered in the electrolysis of solutions of cobalt sulphate to which had been added a slight excess of ammonia, and in solutions of chromium sulphate containing a slight excess of sodium hydroxide. These gave deposits of hydroxide on the anode. Zinc cyanide, redissolved in a slight excess of potassium cyanide, gave a deposit of zinc cyanide on the anode, and between certain values the current was always unsteady.

Anodic films were obtained in the electrolysis of solutions of aluminium sulphate, stannic chloride, and stannous chloride in sodium hydroxide, but these were very loose and did not impede the current. Lead acetate in sodium hydroxide solution gave a deposit of lead peroxide which was not sufficiently readily soluble in the solution to produce periodicity. Cuprous chloride in hydrochloric acid gave cupric chloride as a soluble anodic product. Mercuric potassium iodide gave mercuric iodide and iodine at the anode and would probably have served admirably for the purpose of obtaining a periodic electrolysis, but further experiments were not carried out since the iodine alone could account for the effect. Silver chloride in ammonia gave a loose deposit of silver chloride at the anode, which was unsuitable for the present purpose.

Anodic deposits were not produced when ammoniacal solutions of cadmium nitrate or of zinc sulphate were electrolysed, or in the electrolysis of sodium zincate solutions.

Experiments on the electrolysis of mercury potassium cyanide solutions and of cadmium cyanide gave well-marked periods where the seat of the periodicity was the *cathode*, at which a periodic evolution of hydrogen was visible. These are the first examples of periodicity at the cathode that the author has observed, and attention is being directed to them.

Summary.

Periodic changes in potential and in current strength were observed between certain current densities in the electrolysis of the following solutions, a platinum cathode being used throughout: Zinc anode with sodium hydroxide, sulphuric acid; amalgamated zinc anode with sulphuric acid; cadmium anode with sulphuric acid, potassium cyanide; mercury anode with potassium cyanide, sodium hydrosulphide, nitric acid; magnesium anode with sulphuric acid; tin anode with sulphuric acid, nitric acid; lead anode with sodium hydroxide.

In each case the conditions of concentration of the solution and current density were worked out and their effects on the nature of the periods determined.

Some of the conditions for periodic phenomena at the anode have been deduced. The conclusions have been verified by experiments on the electrolysis of solutions producing a film at an unattackable anode. Periodic phenomena were observed when the film had equal chances of dissolving and of forming.

The author wishes to express his indebtedness to Dr. J. F. Spencer for his continued interest in the work, and to the Chemical Society for a grant which has assisted its prosecution.

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CCCXL.—*Thionyl Bromide and Besson's Supposed Thionyl Chlorobromide.*

By HORACE ALFRED MAYES and JAMES RIDDICK PARTINGTON.

IN 1891, Michaelis (*Ber.*, **24**, 745) prepared thionyl bromide, apparently for the first time, by the action of bromine on thionylaniline. He described it as a brown liquid, b. p. 136° (decomp.), but was unable to obtain it pure because of the decomposition.

Hartog and Sims (*Chem. News*, 1893, **67**, 82) prepared a small quantity of thionyl bromide by the action of sodium bromide on thionyl chloride. They described it as a deep crimson liquid, $d^{18°}$ 2·68, decomposing at 150°, and so hygroscopic that it had to be kept in sealed tubes. They suggested that its colour was due to the presence of sulphur bromide.

Besson (*Compt. rend.*, 1896, **122**, 320) stated that dry hydrogen bromide has no action on cold thionyl chloride but reacts with it at its boiling point to effect substitution of bromine. He separated the

products by fractionation under reduced pressure and obtained thionyl bromide and thionyl chlorobromide, SOClBr, which he described as a clear yellow liquid, $d^{0°}$ 2·31, distilling under ordinary pressure at about 115°. At temperatures just above its boiling point it decomposed into thionyl chloride, sulphur bromide, bromine, and sulphur dioxide. Thionyl bromide he described as a yellowish-orange liquid, b. p. 68°/4 cm., $d^{0°}$ 2·61, giving Br, 76·35, 76·19% (Calc. : 76·95%). It always contained a little sulphur chloride and was readily decomposed by heat. Together with these products a certain amount of sulphur bromide was always formed. He attempted to prepare thionyl bromide by the action of sulphur dioxide on phosphorus pentabromide, but found that decomposition occurred. Later (*Compt. rend.*, 1896, **123**, 884) Besson prepared these compounds by the action of aluminium bromide on thionyl chloride, cooled in a freezing mixture. The yield was much lower, since considerable heat was evolved and consequently decomposition occurred. He gave the freezing point of thionyl bromide as −50°.

Preparation of Thionyl Bromide.

Several unsuccessful attempts have previously been made to prepare thionyl bromide by the action of sulphur dioxide on phosphorus bromide, and, with the exception of this, all the methods of preparation were examined.

1. *The Action of Sulphur Bromide on Sulphur Trioxide.*—Sulphur trioxide was added to cooled sulphur bromide in quantities calculated from the equation $S_2Br_2 + SO_3 = SOBr_2 + SO_2 + S$, which is analogous to that for the preparation of thionyl chloride. Violent effervescence took place immediately, bromine and sulphur dioxide being given off. The considerable residue, on distillation, gave a small quantity of bromide, the major portion being unchanged sulphur bromide. This method is therefore useless.

2. *The Interaction of Bromine and Thionylaniline.*—Bromine was dropped very slowly, with stirring, into a solution of thionylaniline in light petroleum. A precipitate of tribromoaniline hydrobromide was formed, together with a dark red solution. On distillation, this gave a small quantity of thionyl bromide, $C_6H_5{\cdot}N{:}SO + 3Br_2 = C_6H_2Br_3{\cdot}NH_3Br + SOBr_2$, but the yield was poor and the liquid obtained was difficult to purify.

3. *The Interaction of Aluminium Bromide and Thionyl Chloride.*—Anhydrous aluminium bromide was added to thionyl chloride cooled in ice : the bromide dissolved with considerable evolution of heat, and decomposition occurred. The product was distilled in a vacuum on a water-bath, and the distillate fractionated. Only a small quantity of thionyl bromide was obtained, since much

bromine and sulphur bromide were formed. This confirms Besson's observation that the yield of bromide by this method is poor.

4. *The Action of Potassium Bromide on Thionyl Chloride.*—Dried, powdered potassium bromide was refluxed with 50 c.c. of thionyl chloride on a water-bath for 5 hours. The liquid was distilled in a vacuum on a water-bath, and then fractionated under reduced pressure. A small quantity of liquid, b. p. 50—60°/40 mm., was obtained, the greater part being unchanged thionyl chloride. The action is slow, and the large bulk of solid renders the first distillation in a vacuum very awkward.

5. *The Action of Hydrogen Bromide on Thionyl Chloride.*—Hydrogen bromide, dried by calcium chloride, was passed through thionyl chloride contained in a two-necked flask fitted with a reflux condenser. Both the lead-in tube and the condenser were ground into the necks, since thionyl chloride attacks cork and rubber. Slow reaction took place even in the cold, the liquid becoming red after about ¾ hour. It was necessary to pass the gas for about 10 hours to cause any considerable replacement of chlorine by bromine.

Hydrogen bromide was passed through 50 c.c. of cold thionyl chloride, and also 50 c.c. of boiling thionyl chloride, in each case for nearly 4 hours. On distillation, it was found that about the same amount of thionyl chloride had been changed in each case. This is in direct opposition to Besson's statement that hydrogen bromide has no effect on cold thionyl chloride. All further preparations of thionyl bromide were carried out in the cold.

During this reaction, whether carried out with boiling or cold thionyl chloride, some bromine is always liberated, and hence the fractions obtained on distillation are contaminated with it. It is rather difficult to remove the last traces, but this may be accomplished by repeated distillation.

Although Besson stated that the excess of thionyl chloride could be removed by distillation on a water-bath, it was found that a considerable amount of the bromide was removed at the same time. The product was therefore always submitted to a complete fractionation under reduced pressure in a special distilling apparatus fitted with ground glass joints. It was necessary to protect the manometer by soda-lime tubes fitted in the side-arm leading to it, otherwise the mercury rapidly became corroded. The fractionation was usually carried out at about 200 mm. pressure, since the whole of the liquid then distilled between 50° and 100°; at lower pressures, a considerable proportion of the more volatile fraction was lost. At this pressure the liquid was separated into fractions boiling at 10° intervals between 40° and 100°. After prolonged fractionation, most of the liquid collected in the first and the last fraction. The

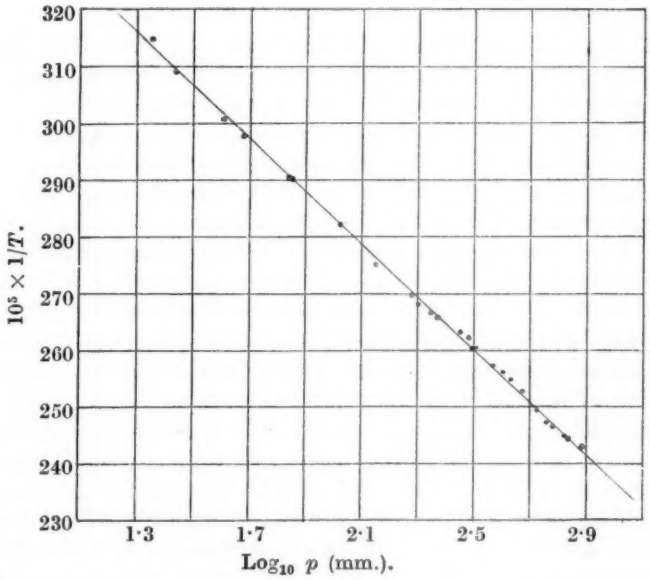
latter was further separated to give pure thionyl bromide and all the residues were united and used for further bromination.

Properties of Thionyl Bromide.

As prepared by method 5, thionyl bromide is a yellowish-orange liquid (Found: Br, 77·11, 76·79, 76·68. Calc.: Br, 76·88%). The analyses were carried out by dissolving a weighed quantity of the bromide in water and precipitation with silver nitrate.

Boiling Points.—The boiling points were determined over the pressure range 22 mm. to 773 mm. The liquid boiled with very little decomposition at 250 mm., but with a considerable amount at 773 mm. This decomposition renders the higher boiling points somewhat inaccurate. These boiling points lie on a smooth curve, and if the values of log p are plotted against the reciprocals of the absolute temperatures, the points lie almost entirely on a straight line (Fig. 1).

FIG. 1.



B. p.	p (mm.).	B. p.	p (mm.).	B. p.	p (mm.).	B. p.	p (mm.).
45°	22	90°	138·5	111°	311	131°	570
50·5	27·5	98	190	111	320	132	601
59	40	99	200	115·5	365	135	660
62·5	47	101·5	219	117	395	136	680
71	67·5	103	233	120	421	138	773
71·5	70	107	274	123·5	471		
81·5	104	109	305	127·5	520		

The b. p. 59°/40 mm. does not agree with Besson's value of 68°/4 cm.; the above value has been checked many times during the distillation of different samples of thionyl bromide and is undoubtedly correct.

Density.—This was determined by using a pyknometer with ground glass caps. Two experiments gave $d_4^{15°}$ 2·698, 2·697. These values do not agree with Besson's value of 2·61, but agree fairly well with that of Hartog and Sims, *viz.*, 2·68, especially as their liquid was not quite pure.

Freezing Point.—The freezing point was determined as — 52° by immersing the liquid in solid carbon dioxide, the temperature being registered by a pentane thermometer.

Molecular Weight.—The molecular weight was determined by the cryoscopic method in benzene. Three determinations with different samples of benzene gave M, 234, 246, and 237 (Calc.: 208). The deviation from the theoretical value is too great to be attributed to experimental error, and also it is consistent. Hence thionyl bromide is associated to the extent of 25% in benzene on the assumption that double molecules are formed.

The Trouton coefficient was calculated from the data already obtained; λ, the molecular heat of vaporisation, was calculated from the equation $\lambda = 4{\cdot}576(\log p_2/p_1)\{T_1T_2/(T_2 - T_1)\}$, where T_1 and T_2 are the absolute temperatures corresponding with the vapour pressures p_1 and p_2. From the straight line obtained by plotting $\log p$ against $1/T$, the following values were taken: $T_1 = 404$, $\log p_1 = 2{\cdot}7624$; $T_2 = 422$, $\log p_2 = 3{\cdot}0024$; hence $\lambda = 10{,}400$ cals. From the curve, the absolute boiling point at 760 mm. is 412·8° (139·7° C.). Hence the Trouton coefficient λ/T_0 has the rather high value of 25·2, which points to association of the liquid.

Surface Tension.—To gain further insight into the molecular complexity of thionyl bromide, surface tension measurements were made at 17° and 25°.

From the mean of two experiments (2·674, 2·669) thionyl bromide was found to have $d_4^{25°}$ 2·672. From this value, and the density at 15°, that at 17° was calculated as 2·692. The surface tension at 17° was found to be 43·71 dynes/cm. by a comparison of the rises of benzene and thionyl bromide in a capillary tube, the value for benzene at 17° being taken as 28·43 dynes/cm. The surface tension at 25° was similarly found to be 43·08, that of benzene being taken as 27·39. The Ramsay and Shields coefficient was therefore — 0·94.

Though these figures cannot be regarded as very accurate, they serve to show that there is some association in liquid thionyl bromide. The ratio of the absolute temperatures corresponding with pressures of 760 mm. and 200 mm. is 412·8/372 = 1·108, whereas according

to Ramsay and Young normal liquids have the value 1·114; association is therefore again indicated.

Chemical Properties.—Thionyl bromide is readily hydrolysed by water with the formation of hydrobromic acid and sulphur dioxide, but, contrary to the statement of Hartog and Sims, it can be kept quite well in a stoppered bottle. About 200 g. of thionyl bromide have been kept in this way for many weeks without undergoing any appreciable hydrolysis.

Decomposition, with formation of sulphur dioxide, bromine, and sulphur bromide, occurs at the ordinary temperature to a very slight extent. It is quite noticeable after a few days, and thionyl bromide which has been kept for some time is always red in colour owing to the presence of free bromine. A tube containing thionyl bromide which had been sealed for 6 months did not appear to have developed any great pressure, although the liquid was dark red. From this it would seem that the decomposition, although quite definite, takes place very slowly. This decomposition occurs readily at temperatures much above 100° so that, at the boiling point under normal pressure, quite one-third of the substance is decomposed by distillation, according to the equation $4SOBr_2 = 2SO_2 + S_2Br_2 + 3Br_2$. Thionyl bromide is a very reactive liquid, attacking both cork and rubber readily. It is soluble in the more inert organic solvents such as benzene, carbon disulphide, carbon tetrachloride, and chloroform, but with acetone it reacts violently to give a vapour having a very irritating effect on the eyes. With organic acids, it forms the acid bromides just as thionyl chloride gives the chlorides. A small quantity was warmed on a water-bath with heptoic acid; considerable effervescence took place, and a product of b. p. *ca.* 186°/760 mm. was isolated. It gave hydrobromic acid and heptoic acid on heating with water, and contained about 35% Br [$CH_3 \cdot (CH_2)_5 \cdot COBr$ requires Br, 41·3%]. It was not obtained pure owing to the limited quantity of heptoic acid available.

Thionyl Chlorobromide.

According to Besson this compound is formed, together with thionyl bromide, when hydrogen bromide reacts with thionyl chloride. Attempts to prepare it in this way were unsuccessful.

Dry hydrogen bromide was passed through thionyl chloride, and the product distilled under reduced pressure. After the unchanged thionyl chloride had passed over, the temperature rose steadily with no interruption, until it attained the boiling point of thionyl bromide. During many preparations, there was never any indication of the formation of a compound intermediate between thionyl chloride and thionyl bromide. On continued fractionation,

the middle fractions always separated gradually to give the chloride and the bromide.

Thionyl chloride was treated with dry hydrogen bromide for a few hours, and the product (75 c.c.) fractionated at 200 mm. pressure; there were finally obtained 26 c.c. of fairly pure thionyl bromide and 35 c.c. of fairly pure chloride (contaminated with some bromine), together with very small quantities of each of the four intermediate fractions, amounting altogether to 10 c.c. These fractions were so small that it was impossible to distil them further. Thus there were recovered 71 c.c. out of 75 c.c. of the brominated product.

From Besson's statements it would be expected that, as the bromide and chloride were present in such proportions, there would have been a considerable quantity of thionyl chlorobromide, but it is obvious from the above experiment that only a very small amount, if any, of chlorobromide was present.

The product from the action of potassium bromide on thionyl chloride was also distilled carefully, and gave results precisely similar to those above.

The aluminium bromide method was unsuitable for this investigation owing to the poor yield and impurity of the product obtained.

Although the above facts offer considerable evidence for the non-existence of thionyl chlorobromide, it seems that the question cannot be settled by any purely chemical method, since the reactions of an equimolecular mixture of thionyl chloride and bromide must necessarily be very similar to those of thionyl chlorobromide. Accordingly, various physical measurements were made, all of which showed that the so-called thionyl chlorobromide is exactly the same as a mixture of the chloride and bromide.

Thionyl chloride was treated with hydrogen bromide, and the product distilled under reduced pressure. From an examination of the boiling point of thionyl "chlorobromide" and those of the bromide and chloride under ordinary pressure, it would appear that the chlorobromide should boil at about 70—80°/200 mm., so this fraction was collected separately. The liquid was analysed for total halogen by the method used for thionyl bromide, and found to contain 30·46% $SOCl_2$ and 69·54% $SOBr_2$, whereas thionyl chlorobromide would have given 36·5% and 63·5%, respectively, corresponding to an equimolecular mixture of the chloride and bromide.

No substance other than thionyl chloride, bromide, or chlorobromide could have been present, since pure hydrogen bromide and pure thionyl chloride were used, and the only by-products, bromine and sulphur bromide, were removed in the distillation, bromine in the first fractions and sulphur bromide in the residue.

A mixture of thionyl bromide and chloride corresponding with the above was prepared containing exactly 30·46% of thionyl chloride. The only possible difference between this mixture and the brominated product would be that the latter might contain some chlorobromide, if it existed, whereas the former might contain only the bromide and the chloride.

The physical properties of these two mixtures were then determined. (The ready hydrolysis of the liquids, combined with their chemical activity, made all work with them difficult, and prevented an accurate determination of the refractive index, for instance.)

Comparison of Physical Properties of Mixtures at 17°.

	Density.	Surface tension.	Viscosity.
1. Brominated product	2·290	40·35	0·01652
2. Mixture of $SOCl_2$ and $SOBr_2$	2·270	40·0	0·01622

These figures agree within the limits of experimental error, which is affected, in addition, by that due to analysis.

These results show that the liquid, which, according to Besson, should contain a large proportion of thionyl chlorobromide, has the same physical properties (density, surface tension, and viscosity) as those of a mixture of thionyl chloride and thionyl bromide containing the same amount of total halogen. Also, the mixture prepared from thionyl chloride and bromide boiled at about the same temperature as the brominated product, and was just as difficult to separate into its constituents by distillation.

No attempt was made to ascertain the variation of the vapour pressure of mixtures of thionyl chloride and bromide with composition, owing to the hygroscopic and chemically active nature of the liquids, but some idea of the nature of this curve was obtained from the manner in which mixtures of the two compounds distilled: the boiling point rose perfectly evenly from that of the chloride to that of the bromide.

Finally, the freezing-point curve of mixtures of thionyl chloride and bromide was investigated. Mixtures of the pure liquids were prepared by weighing, and the freezing point of each mixture was determined with a pentane thermometer. The first few points on the curve were obtained by cooling in solid carbon dioxide, but it was then found necessary to use much lower temperatures and a special cooling bath was applied.

The apparatus consisted of a Dewar vessel containing alcohol and stirred by hand. Immersed in this were two test-tubes, one containing the liquid mixture under consideration, and the other a small plug of cotton wool. A thermos flask, used as a liquid-air reservoir, was fitted with a doubly-bored cork through which

passed two glass tubes. One was a short, right-angled bend connected with a bicycle pump, and the other a long tube dipping into the liquid air and bent so as to pass into the second test-tube in the Dewar vessel. This end was drawn out so that, when the bicycle pump was worked slowly, a fine spray of liquid air was thrown on to the cotton wool. This cooled the alcohol by evaporation, and thus the temperature of the bath was lowered at will. When the temperature fell much below — 100°, the alcohol became so viscous that stirring was difficult, consequently some of the lowest freezing points were not very accurate.

During these experiments the freezing point of thionyl chloride was observed as — 104·5°; it seems that this has never been recorded before. The following table shows the results obtained.

$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.	$SOBr_2$ (%).	F. p.
100	−52°	74·62	−76°	44·82	−96·5°	14·97	−107·5°
94·15	58·6	68·86	79·7	40·04	99	9·06	109
90·77	61·5	67·65	80·9	28·9	104·5	5·29	107 5
83·36	68·9	59·69	85·5	20·8	108	0	104·5
79·8	71·5	50·30	92·5	16·1	108		

All these freezing points were repeated, three determinations of each being made. The necessary correction for emergent stem has also been made.

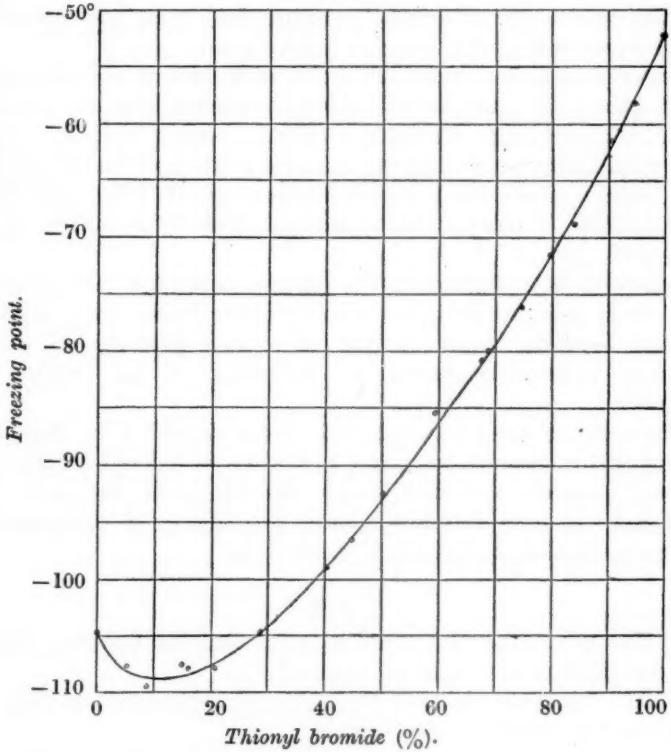
These freezing points plotted against composition (Fig. 2) agree with a simple mixed-crystal curve showing a minimum but no eutectic. It would be possible to draw a curve containing a maximum and two eutectics in the region of 10 to 20% of thionyl bromide, but this would indicate the existence of a very unlikely compound. Moreover, the general shape of the curve is not what would be expected if a eutectic were present, since it is slightly concave, whereas eutectic curves are generally convex. Work in this particular region was found very difficult, and it is considered that the slight irregularities are due to experimental errors. The main object of the experiments was fulfilled, since it is clear that no indication of the existence of the compound SOClBr is evident. The so-called thionyl chlorobromide corresponds with a composition of 63·5% bromide. The freezing-point curve at this point is quite smooth and shows no maximum or break such as would be expected if the chlorobromide were present.

It might be objected that the mixture obtained on bromination of thionyl chloride is not the same as a mere mixture of chloride and bromide. The physical measurements given above suggest, however, that the two types of mixtures are identical, but to remove all doubt the following experiments were carried out.

Hydrogen bromide was passed through boiling thionyl chloride

for some hours, and the product distilled under reduced pressure. The first fractions were rejected, as they contained bromine, but two fractions boiling in the region of 70°/200 mm. were collected. These had been prepared exactly according to the directions of Besson, and should be nearly pure thionyl chlorobromide [Found: (i) 64·09, (ii) 62·21% of thionyl bromide]. The freezing points of these two liquids, taken as before, were: (i) — 82·75°, (ii) — 84·5°. These

FIG. 2.



two points lie almost exactly on the curve, and, further, the figures for the analyses of the fractions show that they should be very nearly pure thionyl chlorobromide.

Thus the liquids obtained on bromination of thionyl chloride are absolutely identical with the corresponding mixtures of thionyl chloride and thionyl bromide. The freezing-point curve shows that there is no chlorobromide in mixtures of chloride and bromide, and hence we may conclude that thionyl chlorobromide is not present in the product formed by the bromination of thionyl chloride.

It only remains to explain the apparent preparation of thionyl chlorobromide by Besson. He describes it as a clear yellow liquid, d^0 2·31, which "distille, sous la pression normale, *aux environs* de 115° C."

The middle fractions obtained during the distillation of brominated thionyl chloride are, after removal of bromine, clear yellow liquids. One fraction, containing 69·54% of thionyl bromide as compared with 63·53% for the "chlorobromide," has d^{17} 2·29, comparing fairly well with Besson's value of 2·31 at 0°. This fraction boiled at about 110—120° at normal pressure, with some decomposition, thus corresponding with Besson's boiling point.

Besson states that thionyl chlorobromide decomposes, on heating much above 100°, into thionyl chloride, sulphur bromide, bromine, and sulphur dioxide: $8SOClBr = 4SOCl_2 + 2SO_2 + S_2Br_2 + 3Br_2$. This would be expected to happen with a mixture of thionyl chloride and bromide, since the latter decomposes above 100°: $4SOBr_2 = 2SO_2 + S_2Br_2 + 3Br_2$, whilst thionyl chloride is stable up to 400—500°.

Besson gives no figures for the analysis of thionyl chlorobromide, and it is noteworthy that Hartog and Sims, who prepared thionyl bromide by the action of sodium bromide on thionyl chloride, apparently found no indication of an intermediate compound.

There seems no doubt that the liquid described by Besson as thionyl chlorobromide is merely a mixture of thionyl chloride and thionyl bromide, and that thionyl chlorobromide has never been prepared. It may be inferred, from the absence of compounds of similar type, that it probably does not exist.

Summary.

1. The properties of thionyl bromide and the freezing point of thionyl chloride have been determined.

2. The evidence showing that thionyl chlorobromide does not exist may be summarised as follows:

(*a*) It is impossible to separate any constant-boiling liquid, other than thionyl chloride and thionyl bromide, from the product of bromination of thionyl chloride with hydrogen bromide.

(*b*) The freezing-point curve shows that no intermediate compound is present in mixtures of thionyl chloride and bromide.

(*c*) Physical properties show that the product of bromination of thionyl chloride is exactly the same as mere mixtures of thionyl chloride and bromide.

(*d*) From (*b*) and (*c*) it is obvious that thionyl chlorobromide is not formed on bromination of the chloride.

In conclusion, the authors wish to acknowledge their indebtedness to Mr. W. H. Patterson for the design of the very convenient type of cooling bath used.

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CCCXLI.—*Parallelism between the Effect of Neutral Salts on the Electrical Charge of Hydrated Manganese Oxides and the Concentration of Hydrogen Ions liberated.*

By BHUPENDRANATH GHOSH.

IT is well known that hydrated manganese dioxide develops an acid reaction in contact with neutral solutions of salts (compare Friend, "Text-book of Inorganic Chemistry," VIII, p. 289). A solid of variable composition, depending on the conditions of preparation, is produced which can be represented as $x\mathrm{MnO_2},y\mathrm{MnO},z\mathrm{H_2O}$.* According to classical conceptions, the acid reaction is conditioned by the relative solubilities of the complex acidic solid and its corresponding salts. A parallel case where, instead of an acid, an alkaline reaction is developed is the action of potassium chloride on silver oxide (Noyes and Kohr, *Z. physikal. Chem.*, 1902, **42**, 336).

It has frequently been suggested that the acidic properties of clays or silica depend on the capacity of the substance to adsorb acids. Mukherjee (*Phil. Mag.*, 1922, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 191) has suggested that the liberation of acid is to be attributed to an interchange between cations in solution and hydrogen ions in the double layer, and he has developed a theory of such reactions based on his theory of adsorption of ions (Faraday Society Discussion, October, 1920) and the electrical double layer. He also states that the interaction of silica with electrolytes cannot be accounted for on the basis of our usual conceptions of ionic equilibrium in heterogeneous systems. On the other hand, Joseph (J., 1923, **123**, 2022; 1925, **127**, 2813) considers that the chemical point of view is sufficient to explain this reaction. Evidently, a change in our usual conceptions cannot be made unless there is strong experimental evidence against them. A detailed study was made of the oxides of manganese of variable composition with a view to obtain decisive evidence on the point. The existence of manganites (*e.g.*, $\mathrm{CaO},5\mathrm{MnO_2}$) corresponding to a definite acid or acids is not questioned; moreover, the substance must, broadly

* The samples obtained in the present work contained traces of potassium.

speaking, behave like an acid, as it contains replaceable hydrogen ions. The question at issue is whether a better explanation of the facts is offered by considerations of solubility or by the conception of an equilibrium between hydrogen ions and cations in the double layer with those in solution. Our observations show that there is a close relationship between the effect of a cation on the electrical charge of the surface and its capacity to liberate hydrogen ions, as postulated by Mukherjee, and that this point of view undoubtedly gives a better explanation of the facts.

Experimental.

Material.—The substance used was obtained by mixing hot solutions of manganous sulphate and potassium permanganate containing a little sulphuric acid; except in one instance, the manganous sulphate was used in slight excess. The composition of the precipitate depends on the conditions of preparation. The approximate compositions of the samples used are :

Sample A, $16MnO_2,3MnO,332H_2O$.
,, B, $7{\cdot}3MnO_2,MnO,114H_2O$.
,, C, $9{\cdot}1MnO_2,0{\cdot}52MnO,92H_2O$.
Sample D, $8{\cdot}2MnO_2,0{\cdot}68MnO$.
,, E, $11MnO_2,1{\cdot}2MnO$.

(Sample C was prepared by using an excess of potassium permanganate solution.)

The first three samples, which were dried in air for 2—4 days, still contained considerable amounts of water; they were kept in stoppered bottles. The last two samples were used for electro-osmotic experiments; they were not dried in air, but were kept in contact with water.

The Stoicheiometric Relationship between the Number of Atoms of Manganese and of Replaceable Hydrogen.—Manganous acid corresponding to MnO_2,H_2O is unstable. The manganites described in the literature correspond to several complex acids, *e.g.*, CaO,MnO_2; $CaO,2MnO_2$; $CaO,5MnO_2$ (compare Friend, *op. cit.*, p. 286). The ratio of the number of acid hydrogen atoms to manganese atoms is therefore variable and depends on the conditions of preparation of the salt. As is well known, in the case of meta- and ortho-acids the potential number of replaceable hydrogen atoms per mol. of the non-metallic oxide is not identical with the actual basicity of the acid. Moreover, in the case of polybasic acids, the extent to which the successive hydrogen ions are replaced by cations depends on the corresponding dissociation constant and the alkalinity of the solution. It was therefore not possible to predict, from the existence of a number of manganites, the basicity of the material employed, especially as the solutions used were not alkaline but acid in reaction (*vide infra*). The number of hydrogen atoms replaceable under

the experimental conditions, which is of interest as indicating the stoicheiometrical relations involved, was determined as follows: A mixture of 4 g. of the sample A and 200 c.c. of a saturated solution of barium nitrate (p_H 6·4—6·6) was thoroughly shaken in a resistance-glass (Pyrex) bottle and then left for 24 hours. A definite volume of the clear supernatant liquid was withdrawn, and its p_H determined by comparison with a set of indicator standards (Clark and Lubs). 200 C.c. of fresh barium nitrate solution were added to the bottle and the process was repeated. The results are in Table I, successive withdrawals usually corresponding to intervals of one day.

TABLE I (Sample A).

Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.
150	2·3	200	4·4	200	5·5	200	6·0
200	2·7	200	4·5	200	5·6	200	6·2
200	3·1	200	4·6	200	5·6	200	6·2
200	3·5	200	4·8	200	5·8	200	6·3
200	3·8	200	5·0	200	5·8	200	6·3
200	4·0	200	5·4	200	6·0	200	6·4
200	4·2	200	5·4	200	6·0	200	6·4

The total acid set free as calculated from the above experiment is equivalent to about 1·46 c.c. of *N*-acid. Hence the number of replaceable hydrogen ions per g.-atom of manganese is 0·145. The results of two similar experiments, using different electrolytes and different samples, are given for comparison in Table II, from which

TABLE II.

Sample.	Amount taken.	Electrolyte.	Total acid set free (in c.c. of *N*-acid).	Number of replaceable hydrogen ions per atom of Mn.
A.	10 g.	Sat. potassium nitrate.	3·3	0·132
C.	25 g.	Sat. barium nitrate.	7·1	0·073

it is seen that C contains a much smaller number of replaceable hydrogen ions per atom of manganese than A. Both samples, however, contain manganous oxide molecules, and, on the assumption that they form manganous manganite or the sesquioxide, which may be taken to have no "potential" acidity, the number of replaceable hydrogen ions per mol. of free manganese dioxide has been calculated (Table III, col. 5).

The ratio (atoms of quadrivalent manganese) : (replaceable hydrogen ions) is widely different in the two cases. Further, for the same sample the number of replaceable hydrogen ions per atom of

TABLE III.

Sample.	Electrolyte.	Ratio of replaceable hydrogen ions to atoms of Mn.	mols. of MnO_2.	free mols. of MnO_2.
A.	KNO_3	0·132	0·156	0·19
	$Ba(NO_3)_2$	0·145	0·172	0·21
C.	$Ba(NO_3)_2$	0·073	0·077	0·082

manganese is somewhat different according as it is estimated by washing with saturated solutions of potassium nitrate or barium nitrate.

From Table I it appears that successive washings cause a regular fall in the hydrogen-ion concentration. An attempt to explain this fall on the basis of the usual chemical conceptions needs the assumption that a solid solution of the complex salt with the corresponding acid is formed, such that the solubility (or rather, activity) of the complex acid decreases, and the solubility (activity) of the salt increases in the way indicated by the variation in the concentration of hydrogen ions. Nothing is known, however, regarding the solubility of either the complex acid or its salts. The salts of alkali metals are very soluble and it is still more difficult to assume that the solid phase contains insoluble alkali-metal salts in equilibrium with a solution which has an acid reaction. The question is really one of the relative solubilities (activities) of the acid and the alkali-metal salt in a state of solid solution, but, in general, the solubilities of the alkali-metal salts are so great compared with that of the acidic substance that a quantitative consideration of the equilibrium conditions strongly points to the conclusion that the usual chemical conceptions are not likely to be of much service.

Generation of Acids in Contact with Neutral Solutions of Salts.—4 G. of the substance and 100 c.c. of a neutral salt solution were treated exactly as before (p. 2607) but the p_H of the supernatant liquid was now determined by *E.M.F.* measurements, using normal calomel electrodes and a potentiometer reading correctly to 0·5 millivolt. The results are in Tables IV and V. About 4 g. of the substance were also shaken with pure water, and the p_H of the water was changed from 6·2 to 5·4, showing that traces of acid were liberated.

TABLE IV (Sample A).

Conc. of electrolyte.	KCl. *E.M.F.* (volt).	Temp.	p_H.	NaCl. *E.M.F.* (volt).	Temp.	p_H.	LiCl. *E.M.F.* (volt).	Temp.	p_H.
N	0·414	32°	2·16	0·414	34°	2·15	0·415	33°	2·17
N/5	0·420	31	2·28	0·427	33	2·37	—	—	—
N/10	0·425	33	2·34	0·433	33	2·47	0·439	33	2·57
N/100	0·435	33	2·50	0·451	34	2·76	0·470	30	3·11

TABLE V (Sample D).

Conc. of electrolyte.	$BaCl_2$. E.M.F. (volt).	Temp.	p_H.	$SrCl_2$. E.M.F. (volt).	Temp.	p_H.	$MgCl_2$. E.M.F. (volt).	Temp.	p_H.
$N/5$	0·407	30°	2·06	0·414	30°	2·18	0·425	30°	2·36
$N/10$	0·410	30	2·11	0·417	30	2·23	0·427	30	2·40
$N/50$	0·417	30	2·23	0·424	30	2·35	0·435	33	2·50
$N/100$	0·422	30	2·31	0·431	33	2·44	0·439	33	2·59
$N/200$	0·437	30	2·56	0·440	33	2·59	—	—	—

The above tables show that the capacity of the cations to liberate hydrogen ions is in the order Ba>Sr>Mg>K>Na>Li. According to the chemical point of view, these results signify that the solubility (activity) of the corresponding complex salts in the solid solution should decrease in the above order for ions of equal valency. From this point of view it is not possible to predict *a priori* that the above order should represent the order of solubilities (activities) of the molecules. On the other hand, Mukherjee's theory predicts this order on theoretical grounds.

Table IV also shows that at high concentrations (about N) the p_H tends to the same limit for all the three univalent cations. (It was not possible to use higher concentrations of electrolytes because of the oxidation of the liberated hydrochloric acid by the manganese dioxide.) From the chemical point of view the p_H values at N concentrations show that the solubilities of the three alkali salts are identical. This conclusion contradicts the assumption of a difference in solubility which it is necessary to make in order to explain the behaviour of these electrolytes at lower concentrations. Within the range of concentrations examined, no manganese could be detected in solution.

With the bivalent cations the higher acidity developed precluded the use of higher concentrations, but probably here also practically the same p_H would have been observed for all of them.

The Adsorbability of Cations as determined from Electro-osmotic Experiments.—In contrast to the chemical point of view, the other theory attributes the liberation of hydrogen ions to the adsorption of cations. This theory also postulates that the adsorbability of a cation determines its capacity to diminish the negative charge of the surface. Electro-osmotic experiments were therefore carried out to determine the order of adsorption of the cations. The apparatus was a modified form of that used by Briggs (*J. Physical Chem.*, 1918, **22**, 256), the straight tube being replaced by a U-tube which was always filled with the precipitate between two marks symmetrically situated one on each limb. The electrodes were connected to the main (220 volts) circuit and the distance between them was

maintained constant. The results are reproducible within 5%; those given in any one table were carried out under identical conditions and with the same apparatus. A different U-tube was used for the observations recorded in Table VIII. The rates of movement of the air bubbles are expressed in cm. per 3 minutes, but they only qualitatively represent the variation in the charge per unit area of the surface.

TABLE VI (Sample D).

	Electrolyte.			
Conc.	LiCl.	NaCl.	KCl.	$BaCl_2$.
0	—	− 9·8	−9·8	− 9·8
N/10000	—	—	—	− 8·3
N/5000	—	—	—	− 5·4
N/3000	−17·7	−16	−7·4	—
N/1000	−16·5	−16·3	−5·4	+ 8
N/500	−14·3	−13·1	−3·8	+13
N/250	−13·4	−11·7	−3·0	+16·7
N/125	—	—	—	+14·5

TABLE VII (Sample E).

	Electrolyte.			
	$BaCl_2$.	$SrCl_2$.	$MgCl_2$.	KCl.
	−10·8	−10·8	−10·8	−10·8
	—	−10·5	−11·0	—
	—	− 9·2	−10·0	—
	—	—	—	—
	+ 3·6	− 0·6	− 7·7	—
	+11·0	+ 3·0	− 4·0	—
	—	+ 7·1	− 0·2	− 1·8
	—	+ 9·6	+ 1·1	—

TABLE VIII (Sample E).

	Electrolyte.				
Conc.	KCl.	KNO_3.	K_2SO_4.	K_2HPO_4.	KOH.
0	−8·2	−8·2	−8·2	− 8·2	− 8·2
N/1000	−6·5	−7·5	−8·8	− 8·9	− 9·3
N/500	−5·7	−6·8	−8·7	−10·3	−11·4

From these tables certain conclusions may be drawn: (1) Hydrated manganese oxides carry a negative charge in contact with water. (2) Hydroxyl ions increase the negative charge markedly. (3) The capacity of the cations to decrease the negative charge of the surface is in the order Ba>Sr>Mg>K>Na>Li, which is the same as the order of their capacity to liberate hydrogen ions. (4) In the case of lithium and sodium chlorides, at low concentration the negative charge increases. (5) The bivalent cations reverse the charge of the surface. In the case of magnesium chloride, there is evidence of a slight increase in the negative charge at very low concentrations; in that of barium chloride (Table VI), after the reversal of the initial sign in the charge of the surface, the positive charge reaches a maximum and then falls again. (6) The reversal of charge with bivalent cations for the two samples examined occurs between concentrations N/3000 and N/125. It has already been observed that the concentration of the liberated hydrogen ions continues to increase up to a concentration of 0·2N of the bivalent electrolytes, *i.e.*, hydrogen ions continue to be liberated even after the surface has become positively charged. (7) From the experiments with potassium salts of various acids it is seen that the

negative charge of the surface depends on the nature of the anions, thus showing that some of the anions are adsorbed.

The Adsorption Theory and the Liberation of Hydrogen Ions by Cations.—It follows from the theory of electrical adsorption (Mukherjee, *loc. cit.*) that the adsorbability of cations by a negatively-charged surface is determined by their valency, mobility, and hydration, provided that the atoms on the surface do not react chemically with the cations, either through primary, secondary, or residual valencies. It is at once possible to deduce from this theory that the adsorbability of the cations used should be in the order Ba>Sr>Mg>K>Na>Li, which agrees notably with that observed in the electro-osmotic experiments and in the liberation of hydrogen ions.

It has been remarked already that the bivalent cations reverse the electrical charge of the surface. On Mukherjee's theory, one must assume that the point-charges which constitute the negatively-charged primary sheet of the double layer must be univalent ions. When a barium ion is fixed on any of these point-charges, its corresponding hydrogen ion will be displaced. The surface at this point will have a net positive charge consisting of the original primarily-adsorbed univalent negative ion and the electrically-adsorbed bivalent cation. In the mobile sheet of the double layer one of the partner chlorine ions of the barium ion will take the place of the hydrogen ion which has passed into the bulk of the solution. The displaced hydrogen ion will have as its partner in the solution the other chlorine ion of the barium chloride molecule. One adsorbed bivalent cation thus displaces one hydrogen ion. Also, when the negative charge of the surface becomes zero and the surface begins to get positively charged, only half of the initial "uncovered" primarily-adsorbed negative ions are covered with bivalent cations and in the mobile sheet there will be cations (including hydrogen ions) and anions in equivalent quantities. A further increase in the concentration of bivalent cations will liberate fresh quantities of hydrogen ions. On the other hand, from purely chemical considerations one would expect that one barium ion would combine with two univalent negative ions on the surface and thus displace two hydrogen ions. The concentration of liberated hydrogen ions for the same molar concentration of a salt thus represents the amounts of cations adsorbed, and the order of adsorption of these cations is the same as their capacity to liberate hydrogen ions, *viz.*, Ba>Sr>Mg>K>Na>Li.

The fact that at higher concentrations potassium, sodium, and lithium ions set free hydrogen ions at identical concentrations can also be easily explained by this theory. If it is assumed that the

number and the nature of the univalent anions primarily adsorbed per unit surface do not change on the addition of an electrolyte, then the main interaction between the ions in the double layer and those in solution will be a replacement of the hydrogen ions in the double layer by cations in solution. Hydrogen ions may be displaced by a cation through its penetration into the mobile sheet of the double layer or through its electrical adsorption. It has just been seen that one cation fixed on the surface by electrical adsorption displaces, irrespective of its valency, one hydrogen ion from the double layer. Besides these electrically-adsorbed cations there may be present in the double layer a number of cations simply as a result of their osmotic pressure in the bulk of the solution. The double layer as a whole is electrically neutral, and, since the cations must carry a charge equivalent to that of the primarily adsorbed anions, the total amount of charge carried by cations of all sorts in the double layer (under the above assumption) must remain constant. As the proportion of metallic cations to hydrogen ions in the double layer increases, a slight further replacement will increase the ratio more and more rapidly. Consequently the rate of increase of the concentration of hydrogen ions diminishes rapidly with increasing concentration of salts, and at high concentrations a limiting value of the hydrogen-ion concentration is reached which, as has been observed, is practically the same for the three alkali-metal cations.

Similarly, the decrease in the hydrogen-ion concentration in the successive washings recorded in Table I should be referred to the same cause. As the washing progresses, a further small replacement of hydrogen ions in the double layer by metallic ions changes at an increasing rate the ratio of the metallic ions to hydrogen ions.

The equilibrium is thus between the ions in the double layer and those in solution. A change in the ratio of the ions in one produces a change of the ratio in the other.

Analytical Measurement of the Adsorption of Anions and Cations.—The development of acidity has been referred to the adsorption of cations. It has also been seen from electro-osmotic experiments that anions are adsorbed. The adsorption theory assumes that anions are primarily adsorbed on the surface. Electro-osmotic experiments have shown that marked adsorption of hydroxyl ions takes place. It is likely that other anions are also adsorbed. Analytical measurements were undertaken to determine the magnitude of the adsorption of cations and anions. In calculating the adsorption of anions, correction has been made for the diluting effect of the water of hydration (compare Wo. Ostwald and Izagguire, *Kolloid Z.*, 1919, **30**, 279; Mukherjee, *J. Indian Chem. Soc., loc. cit.*).

4 G. of the substance and 100 c.c. of a salt solution were shaken

as before, and the concentration of the alkali metal in the solution was estimated as sulphate. The amount adsorbed (corrected for hydration) is given in Table IX, col. 3, and the acidity of the solution

TABLE IX (Sample A).

Electrolyte.	Concentration.	Cation adsorbed (g.-atom × 10^3).	Hydrogen liberated (g.-atom × 10^3).
KCl	N	0·82	0·69
,,	$N/5$	0·51	0·53
,,	$N/10$	0·44	0·46
NaCl	N	0·69	0·67
,,	$N/5$	0·39	0·42
,,	$N/10$	0·29	0·33
LiCl	N	0·52	0·68
,,	$N/10$	0·28	0·26

in col. 4; it follows from these that, within the limits of experimental error, the number of cations adsorbed is equal to the number of hydrogen ions liberated, *i.e.*, the adsorption of cations is mostly the result of an exchange with hydrogen ions. This does not exclude the possibility of anions being adsorbed in much smaller but appreciable amounts. It has already been concluded from the electro-osmotic experiments that anions are adsorbed.

It will be seen from Table X that the adsorption of anions can be demonstrated when acids are used, for in this case there is no question of exchange of cations and the decrease in hydrogen-ion concentration should be attributed to the adsorption of both anions and cations. The potassium, which is present in traces in the samples (p. 2605), is set free in contact with acid, but not with pure water, and is the result of exchange with hydrogen ions; in the case of sulphuric acid solutions, it was estimated as sulphate, and in the case of other acids it was assumed that the potassium was exchanged for its equivalent of hydrogen ions in the solution. 5 G. of the sample were shaken with 50 c.c. of acid solution and left undisturbed for 24 hours; a definite volume of the clear supernatant liquid was withdrawn and titrated with standard alkali.

TABLE X (Sample C).

Acid.	Initial conc. (g.-mol. per litre).	Conc. corrected for dilution by water.	Final conc. after adsorption.	Potassium exchanged (g.-atoms) × 10^5.	Acid adsorbed (g.-equivs.) × 10^5.
HNO_3	0·2	0·188	0·184	9	11
,,	0·1	0·094	0·092	8·2	1·8
H_2SO_4	0·1	0·094	0·089	9	41
,,	0·05	0·047	0·043	8·2	31·8
H_3PO_4.*	0·1	0·094	0·079	9	141
,,	0·05	0·047	0·039	8·2	71·8

* In the above calculations, this acid has been regarded as dibasic.

Even when allowance is made for the disappearance of the hydrogen ions through exchange with potassium ions, it is seen that the adsorption of the acid, although much smaller than the amount of acid set free in the other experiments, is quite noticeable. The adsorption of different acids from g.-molar concentrations is in the order $H_3PO_4 > H_2SO_4 > HNO_3$. The same order has been noticed for the effect of potassium salts of these acids on the negative charge of the surface. Both these effects being considered, the adsorption of these anions seems to be proved beyond doubt.

Summary.

(1) The interaction of manganese oxides with neutral salts can be satisfactorily accounted for by the adsorption theory of Mukherjee.

(2) In agreement with this theory, the capacity of the different cations to liberate hydrogen ions is in the order Ba > Sr > Mg > K > Na > Li, which is the same as that obtained from electro-osmotic experiments and represents their capacity to neutralise the negative charge of the surface.

(3) The bivalent cations reverse the sign of the charge of the surface, showing that the primarily adsorbed ions are univalent. The electrical adsorption of one bivalent cation will therefore liberate one hydrogen ion. In addition, hydrogen ions are probably replaced by cations penetrating into the mobile sheet of the double layer on account of their osmotic pressure.

(4) The adsorption of acids and the primary adsorption of anions have been demonstrated.

This work has been made possible by the award of a research scholarship by Sir J. C. Bose, C.S.I., F.R.S., D.Sc., Director of the Bose Institute, and I cannot too strongly express my grateful thanks to him for his kind interest and for the facilities he has provided. I am also indebted to Prof. J. N. Mukherjee for helpful suggestions.

BOSE INSTITUTE, CALCUTTA. [*Received, July 7th*, 1926.]

CCCXLII.—*Examination of an Ancient Egyptian (Tut-ankh-Amen) Cosmetic.*

By A. CHASTON CHAPMAN and H. J. PLENDERLEITH.

THE discovery by Dr. Howard Carter of a sealed cosmetic jar of calcite among the many objects of interest in the tomb of Tut-ankh-Amen at Luxor presented a unique opportunity for the examination of an ancient fatty substance which had not entirely decomposed

in the process of time. The tomb itself had remained sealed from the outside air for more than 3300 years, and when opened in 1922 the introduction of sterile swabs failed to indicate the presence of any bacteria. It was therefore of much interest to examine this ancient fatty material with a view to ascertain what changes it had undergone in this sterile environment and, if possible, to collect data which might shed some light upon its probable source.

The jar had been sealed by natural agency, the changes in temperature and moisture having caused certain salts, nearly always associated with Egyptian objects of antiquity, to crystallise round the lid and so to form a hard, protective incrustation.

When the jar was opened by Dr. Carter a considerable quantity of cosmetic was found inside (about 450 g.). This was rather sticky, and presented the appearance of a heterogeneous mixture consisting of yellow nodules together with a chocolate-coloured substance. It melted, in part at least, at the heat of the hand, emitting a faint yet distinctive odour. This odour was to us at first suggestive of that of coconut, but has been variously described since either as resembling that of the flowers of broom, or as being rather valerianaceous in character. The cosmetic had a decidedly fatty smell, but certainly not that characteristic of advanced rancidity. A careful microscopical examination failed to reveal any traces of vegetable fibre or other organised structures.

It is of interest in this connexion that a fat found in Egyptian jars protected by thick mud layers has been described by Petrie and Quibell (" Naquada and Ballas," 1895, p. 39) as dating from a much earlier period of Egyptian history and possessing the external characters at least of the specimen under discussion. The Naquada fat, however, was found to contain vegetable fibre when examined under the microscope. Although the histological examination of the debris proved wholly inconclusive in the hands of Dr. Thistelton-Dyer at Kew, these investigators seem convinced that the presence of fibre in the fat is indicative of its vegetable origin—a conclusion which is not beyond question, having regard to the fact that fats are stated on good authority to have been preserved by the Egyptians by rolling them in vegetable fibre. While Petrie and Quibell state that the nature of their specimen is not yet certain, they conclude that the only source known for it would be one of the vegetable butters, *e.g.*, from Bassia (Shea butter) or the oil palm. It seems unlikely, however, as pointed out later, that the odorous constituents of such fats would be stable enough to withstand the action of oxygen and moisture for such a prolonged period. It should be mentioned that excavators are decided in stating that this smell of coconut is often noticeable in specimens freshly excavated, and this suggests

that it might be due to an odorous product of decomposition of such substances as fats, resins, or balsams.

The Tut-ankh-Amen specimen was largely organic in nature but left a decided residue on ignition consisting mainly of calcium carbonate. Neither nitrogen nor sulphur was present.

General Proximate Analysis.

Fatty matters soluble both in light petroleum and in ether	59·1%
Fatty matters soluble in ether, but practically insoluble in light petroleum	28·6
Matters soluble in alcohol, but insoluble in ether	0·9
Matters soluble in water, but insoluble in alcohol	4·4
Matters insoluble in any of the foregoing solvents	4·7
Moisture (loss on drying at 105°)	2·3
	100·0

The total fatty matters extracted by ether, and amounting to 87·7%, had an acid value of 252·6, an iodine value of 4·5, contained only a trace of unsaponifiable matter, and left 0·4% of ash on ignition. There was also present in it 5·46% of free and combined glycerol, which is equivalent to 4·8% on the cosmetic itself. The cosmetic left on ignition 2·04% of ash.

Fatty Matters Soluble in Ether and Light Petroleum.—The portion of the fatty matter which was soluble both in ether and in light petroleum consisted of a white, crystalline solid, having about the same consistency as palmitic and stearic acids and resembling them in appearance. This retained the odour of the original cosmetic, which now resembled still more closely that of coconut. A portion of this fat gave the following results: Reichert value, 0·9; Polenske value, 0·5; acid value, 214·4.

Fatty Matters Soluble in Ether, but Insoluble in Light Petroleum.—This portion was softer than the preceding portion, showed but little tendency to crystallise, and had a distinct yellow colour. It had an acid value of 331·5 and had only a very slight coconut odour.

Matters Soluble in Alcohol, but Insoluble in Ether or Light Petroleum.—These consisted of a reddish-brown, viscous material, possessing no distinctive odour. The amount was so small that a separate examination was impossible.

Matters Soluble in Water.—This portion was left on evaporation of the water as a translucent, brown, resinous substance, resembling shellac in appearance, and consisted chiefly of calcium salts. On the addition of dilute hydrochloric acid to its aqueous solution, a precipitate was formed which gradually coalesced, forming a sticky, brown mass. This was readily soluble in alcohol, but almost completely insoluble in ether.

Matters Insoluble in Ether, Alcohol, or Water.—This fraction, when

dried, was a brown, amorphous powder, free from odour; on ignition it left 31% of mineral matter, consisting almost entirely of calcium carbonate. When it was treated with dilute acid there was no decided effervescence, but on warming, decomposition apparently occurred, and an acidic substance was formed which was insoluble in water and softened on warming. This acid was insoluble in ether, but was fairly readily dissolved by hot alcohol, separating on cooling as a brown sludge.

A consideration of the above results appears to indicate that the constituents of the cosmetic may be roughly divided into two classes: (*a*) the fatty matters soluble in ether, and (*b*) matters of a resinous character.

It will be seen from the iodine number that the fatty acids are, as might have been anticipated, almost entirely saturated in character. The examination of the fatty matter shows it to contain fatty acids having a high neutralisation value, *i.e.*, the acids are either polybasic or of low molecular weight.

The glycerol is largely, if not entirely, in the free condition, and doubtless this accounts to some extent for the moist character of the cosmetic.

The portion of the material which, although soluble in ether, is almost insoluble in light petroleum, appears to consist of "oxidised" acids, *i.e.*, acids containing two or more hydroxyl groups in the molecule. These are characterised by their relative insolubility in light petroleum, their high neutralisation value, and their relatively great solubility in water.

It is highly probable that these acids have been formed in process of time by oxidation of unsaturated acids present as glycerides in the original fat. Such substances are, in fact, known to be formed when, *e.g.*, oleic acid is oxidised by means of air, and this action would no doubt account for the absence of unsaturated products and for the high acidity. The assumption, which seems probable, that the whole of these acids has been formed in this manner would point to the presence in the original cosmetic of about 25—30% of olein or other unsaturated glycerides. It may be mentioned in this connexion that the adipocere formed in the case of animal bodies which have been buried for a considerable time has been found to consist largely of palmitic and stearic acids, together with oxidised acids, oleic acid being absent. The Reichert and Polenske figures (*vide supra*) indicate that the amount of steam-distillable, low molecular-weight, fatty acids is so small as to preclude the presence of any appreciable quantity of a fat such as coconut fat or palm-kernel oil. It is, of course, just possible that such acids may have been decomposed in the course of time, but having regard to their

known stability, and to the persistence of the glycerol, this seems very unlikely.

Further evidence of the presence of oxidised acids is to be found in the fact that the so-called "saponification value" of the separated fatty matters is very considerably in excess of the acid value, *i.e.*, the number representing the amount of alkali required for the neutralisation of the acids actually present as such. Inasmuch as the greater part, at least, of the glycerol would appear to be in the free condition, this difference can only be accounted for by the presence of a considerable proportion of acid anhydrides. Lewkowitsch (*Analyst*, 1902, **27**, 139) and other observers have directed attention to this point, and in the case of the oxidised acids from blown oils, such as rape, cotton-seed, maize, etc., differences of from 15 to more than 40 units have been recorded, and this in the acids when freshly formed. There can be little doubt that over so long a period of time the difference in the case of a material such as this cosmetic would be even greater.

In the next place, the cosmetic was very carefully examined with the object of ascertaining the nature of any unsaponifiable matter present. It is, of course, well known that the presence solely of cholesterol in a fat or oil is very generally regarded as indicating its animal origin, whilst the presence of other sterols, chiefly phytosterol, is indicative of a vegetable product. As large a proportion of the fat as possible was saponified, and the very small amount of unsaponifiable matters extracted with great care, but this was found to be entirely free from cholesterol, phytosterol, or any other similar crystalline substance. This is not altogether surprising, since it is known that these sterols undergo decomposition and tend to disappear in process of time. It is, however, disappointing inasmuch as a definite result would, of course, have gone a long way towards deciding whether the fat originally present in the cosmetic was of animal or vegetable origin. Incidentally, it may be observed that the very small amount of unsaponifiable matter obtained showed the absence of matters of a waxy nature, since the unsaponifiable matters in the waxes are, generally speaking, of a very stable character. An attempt was next made to obtain some information as to the identity of the saturated fatty acids present in the cosmetic.

A portion of the original material (70 g.) was esterified with methyl alcohol, and the resulting methyl esters (60 g.) were fractionally distilled at 15 mm., portions being collected as follows:

Fraction 1.	Temp.	115—128°	2·49 g.	
,, 2.	,,	128—154	4·93	
,, 3.	,,	154—182	10·72	57·97 g.
,, 4.	,,	182—205	17·72	
,, 5.	,,	205—220	17·52	
Residual tarry matter			4·59	

Fractions 4 and 5 were redistilled, portions being collected at 195—205° and 210—220°, respectively, and all the fractions were then hydrolysed by caustic soda, and the resulting sodium salts decomposed with hydrochloric acid. The free acids so obtained were crystallised from ethyl alcohol repeatedly until sharp melting points were obtained where possible. It was found that the melting points of the acids obtained from fractions 5, 4, and 3 corresponded with those required for stearic, palmitic, and myristic acids, respectively, whilst the melting points for the acids obtained from fractions 2 and 1 could not be rendered sharp by repeated crystallisation, but were located over a range higher than the melting points of lauric and capric acids, respectively. The coconut odour persisted and was decided in the case of the acids from fractions 2 and 3.

The above results do not, unfortunately, enable us to form a definite opinion as to the nature of the fat or fats originally employed, or even to say with certainty whether they were of animal or of vegetable origin. On the whole, we are inclined to regard the chemical evidence as supporting the view that the fat was of animal character, since it does not seem probable that any vegetable fat with the small proportion of olein this appears originally to have contained would have been available. The chemical evidence, generally, would seem to exclude coconut or palm-kernel oils.

Having regard to all the results, it appears probable that the cosmetic consisted of about 90% of a neutral animal fat with about 10% of some resin or balsam.

The large proportion of calcium present is evidently due to the action of the liberated acids on the walls of the containing vase. The smell of the material, which is one of its most characteristic features, is very probably due to odorous substances formed in process of time from the resins or balsams employed. The odorous constituents of coconut, so far as these are known, are of a kind which would scarcely be likely to have resisted the destructive effect of oxygen and moisture over so long a period, and it is much more likely that the substance or substances formed as the result of oxidation changes would have greater stability.

In conclusion, we desire to express our warm thanks to Dr. Howard Carter for the privilege of examining this specimen, and to Dr. Alexander Scott for his kind assistance in furthering the investigation.

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[*Received, August 14th*, 1926.]

CCCXLIII.—*The Hydrates of Manganous Oxalate.*

By Norman Henry Chamberlain, John Hume, and Bryan Topley.

In the course of experiments on the rates of change of metastable systems consisting of salt hydrates with their saturated solutions, determinations have been made of the solubility curves and densities of the two known hydrates of manganous oxalate. This salt forms a dihydrate, stable in contact with its saturated solution between 0° and 100°, and a trihydrate, unstable over this range.

Preparation of the Hydrates.—The dihydrate was prepared by two methods: (1) by the action of potassium permanganate on oxalic acid (Coltman, *Ind. Eng. Chem.*, 1924, **16**, 606); (2) by loss of water from the trihydrate. No difference was observed in the properties of the dihydrate prepared in these two ways. The trihydrate was obtained by mixing ice-cold dilute solutions of manganous sulphate and oxalic acid, the former being in excess; the mixture was kept at 0°, and under these conditions a crystalline product separated in 12 hours. This was filtered off and washed thoroughly with ice-cold water immediately before use.

Solubility Determinations.—The oxalate content of the saturated solution was determined by titration with potassium permanganate which had been standardised on potassium hydrogen oxalate, sodium oxalate, and the dihydrate, $MnC_2O_4,2H_2O$.

Saturation of the solution was effected by mechanical stirring in a flask immersed in a thermostat; samples were removed for analysis by filtration through an asbestos filter attached to the point of a pipette. No difficulty was experienced in the case of the dihydrate, as stirring could be continued until a constant value was obtained. In the case of the trihydrate there is an obvious difficulty in that decomposition is concurrent with the process of dissolution. The true saturation value can be obtained by working under conditions such that the rate of dissolution is much greater than that of recrystallisation of the solute as dihydrate. Now, direct experiment in a dilatometer showed that the rate of decomposition exhibits a pronounced induction period; *e.g.*, at 25° only 1% of the trihydrate decomposes in the first 5 hours, although after 50% of the trihydrate has changed into dihydrate, the rate of decomposition is 1% in 10 minutes. The corresponding figures at 36° are 1% in the first 11 minutes and 7·6% in 10 minutes. Accordingly, at the higher temperatures, an attempt was made to saturate the solution before the induction period was completed by making a thick suspension of the trihydrate crystals in water

and agitating this by a very rapidly rotating mechanical stirrer. During the induction period, the ratio of the surfaces of dihydrate to trihydrate crystals is very small, and therefore it was assumed that, so long as constant results could be obtained within the period of induction, these represent the true solubility. In this way values up to 30° were obtained.

Results.—The averages of the values found at each temperature are given in the table; in no case did the individual values differ by more than 1% among themselves. The solubilities (*s*) are expressed as g. of anhydrous manganous oxalate in 100 g. of saturated solution.

Dihydrate.				Trihydrate.			
t.	*s.*	*t.*	*s.*	*t.*	*s.*	*t.*	*s.*
0·0°	0·0198	25·0°	0·0308	0·0°	0·0326	20·1°	0·0582
6·3	0·0225	30·3	0·0335	6·3	0·0388	25·0	0·0669
12·8	0·0256	36·0	0·0369	12·8	0·0476	30·0	0·0769
20·1	0·0285						

No measurements of the solubilities of the trihydrate are recorded in the literature; those of the dihydrate have been determined by Hauser and Wirth (*J. pr. Chem.*, 1909, **79**, 358), who found 0·0312 g. of MnC_2O_4 per 100 g. of solution at 25°, and by Chatterjee and Dhar (*J. Physical Chem.*, 1924, **28**, 1009) at 36° and 93°. These authors found 0·0377 at 36° and 0·0813 at 93° (results re-calculated to g. per 100 g. of solution); thus their value at 36° is 2·1% higher than ours. However, it would seem not improbable that the cause of the discrepancy is the presence of a small amount of trihydrate in the dihydrate which they prepared by precipitation at 30°, since at this temperature the precipitate obtained consists at first of a mixture of the two hydrates; the fact that their product gave analytical results in agreement with the formula $MnC_2O_4,2H_2O$ is not significant in this connexion, since, on drying the sample for analysis, the change into dihydrate would be completed. On the other hand, at 93° any trihydrate present at the beginning of the solubility determinations would very rapidly change into dihydrate, so that the value obtained at this temperature would not be too high from this cause; moreover, when the solubility curve of the dihydrate is extrapolated to 93°, by a formula analogous to Ramsay and Young's vapour-pressure formula, a value is obtained in agreement with the result of Chatterjee and Dhar.

In connexion with measurements of the rate of change of the trihydrate into the dihydrate, it is of interest to know the (hypothetical) equilibrium temperature for the system trihydrate–dihydrate–saturated solution.

An estimate of this temperature can be made by extrapolating the solubility curves below 0° by means of the Ramsay and Young relationship

$$T_1/T_2 = T_1'/T_2' + c(T_1 - T_1')$$

where T_1 and T_1' are, respectively, the absolute temperatures at which the trihydrate has the same solubility as the dihydrate at T_2 and T_2', and c is a constant. On plotting T_1/T_2 against $(T_1 - T_1')$, a straight line is obtained, giving $c = -0{\cdot}002301$; the transition temperature T_0 is then given by the formula

$$T_0 = \{T_1'(cT_2' - 1) + T_2'\}/cT_2'.$$

In this way, the transition temperature is found to be $-40{\cdot}6°$.

Alternatively, the solubility curves may be extrapolated by means of a formula of the type

$$\log_{10} s = A - B/T - C \log_{10} T$$

(the form of which results from the assumption that both the heat of solution and the van 't Hoff factor i remain sensibly constant over the temperature range considered), where A, B, and C are constants, and T is the absolute temperature corresponding to the solubility s. In this case, the transition temperature is calculated from the equation

$$0 = (A - A') - (B - B')/T_0 - (C - C') \log_{10} T_0,$$

where A', etc., refer to the trihydrate, and A, etc., to the dihydrate. The solubility parameters obtained from the curves were:

Trihydrate: $A' = -26{\cdot}8626$; $B' = -222{\cdot}82$; $C' = -10{\cdot}080$.

Dihydrate: $A = -8{\cdot}9868$; $B = +201{\cdot}42$; $C = -3{\cdot}2944$.

The discrepancy between values of s calculated from these figures and the experimental curves is nowhere greater than $0{\cdot}004s$. The transition temperature obtained in this way is $-41{\cdot}7°$; and therefore it would seem probable that it lies in the neighbourhood of $-41°$.

Determinations of the Densities of the Hydrates at 0°.—The density of each of the hydrates was determined as follows: A calibrated specific gravity bottle was filled at 0° with a saturated solution, together with a quantity of the crystals, and weighed. The total manganous oxalate content of the bulb was found by titration with $N/10$-potassium permanganate. The amount of manganous oxalate in solution was calculated from a knowledge of the concentration and density of the saturated solution, and the weight of the hydrate was thus obtained by difference. These data, together with the weight of the bulb filled with saturated solution, determine the density.

Density of dihydrate at 0° = 2·2946
" saturated solution at 0° = 1·0001
" trihydrate at 0° = 1·9930
" saturated solution at 0° = 1·0002

A check on the accuracy of these results was obtained by measuring in a calibrated dilatometer the change in volume at 0° corresponding to the decomposition of trihydrate into dihydrate. Allowance was made for the difference in solubility of the two hydrates at 0° (Found: −0·0173 c.c. per g. of $MnC_2O_4,3H_2O$. Calc. from the densities: −0·0176 c.c.).

THE UNIVERSITY, LEEDS. [*Received, July 28th,* 1926.]

CCCXLIV.—*The Dielectric Constants of Some Liquids and Liquid Mixtures.*

By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

IN the course of an investigation into the nature of solution it became necessary to examine the physical properties of a number of binary mixtures of organic liquids. Amongst other properties, the dielectric constants of such mixtures came under review. A certain amount of data had already been placed upon record (Linebarger, *Z. physikal. Chem.*, 1896, **20**, 130; Philip, *ibid.*, 1897, **24**, 18; Schultze, *Z. Elektrochem.*, 1912, **18**, 77), but it seemed desirable to examine particularly certain pairs of liquids the admixture of which had been observed to be attended by interesting changes in temperature and in density. It is here proposed to give an account of the method of measurement and the results obtained; a discussion of these results in their relation to other physical properties is deferred until further data are available.

The method of measurement was substantially that previously described (Sayce and Briscoe, J., 1925, **127**, 315; Sayce, *J. Scient. Instr.*, 1926, **3**, 116), but improvements have been made in the apparatus which add much to its convenience and speed of operation. Thus, both the galvanometer scale and the scale of the condenser C_V (J., *loc. cit.*) have been brought into the field of vision of the reading telescope and the movements of both the oscillator condenser C_2 and the condenser C_V are now controlled by dials permitting of extremely fine adjustment. Errors due to sudden variations of atmospheric temperature are minimised by enclosing C_V and the bank of condensers, C_a to C_l, in wooden boxes lined with stout copper, and the inconvenience of working in a darkened thermo-

static laboratory has thus been removed except in determinations of the utmost precision.

In the present case, it was considered unnecessary to make use of the full accuracy of which the method was capable; therefore an economy of dielectric and a saving of time were effected by the use of a much smaller dielectric container, which took the form

FIG. 1.

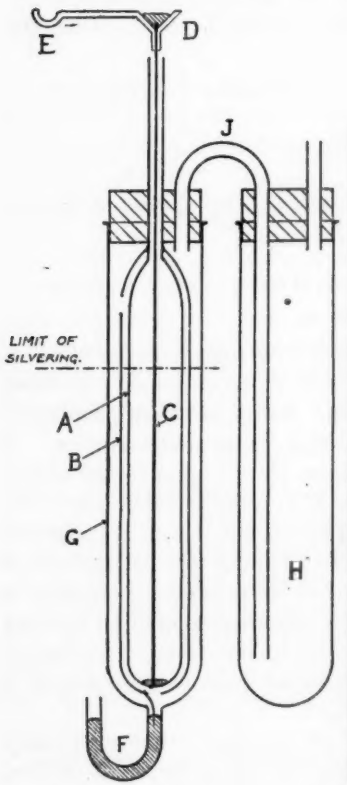
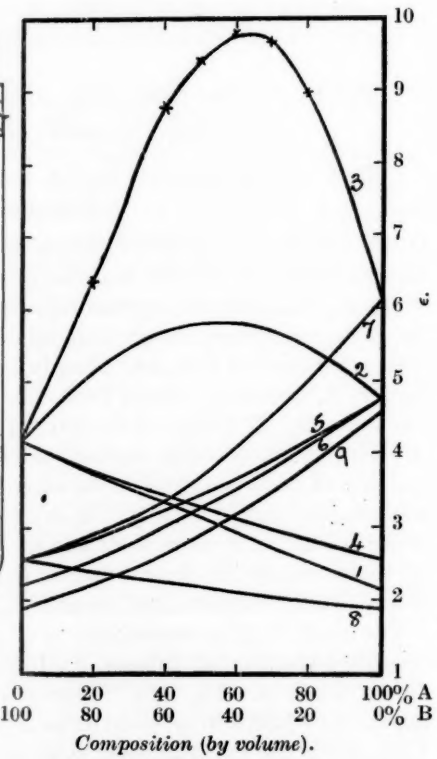


FIG. 2.



shown in Fig. 1. The condenser proper consisted of silver coatings upon two tubes, *A* and *B*, welded together at the top and separated by an annular space of approximately 1 mm. Electrical contact was made with the inner coating by means of a platinum seal in the tip of *A*, to which a stiff copper wire, *C*, was connected by a globule of mercury. A glass cup, *D*, containing mercury, was cemented to the top of *C* and provided the means of connecting

the inner coating of the condenser to the "live" side of the measuring apparatus by transferring a stiff copper wire from the glass rest, E, to the mercury in D. The condenser was contained in an outer jacket, G, having a U-tube, F: a platinum wire sealed into B and dipping into this mercury in F served to make electrical connexion between the silver coating of B and the earthed side of the measuring apparatus. A second vessel, H, similar to G and initially containing the liquid dielectric under examination, was connected to it by the tube J, and the whole apparatus was almost completely immersed in a thermostat.

The measurement of the dielectric constant of a liquid or liquid mixture involved the following operations:

1. 50 C.c. of the given dielectric were placed in H, which was then closed by a cork and drying-tube.

2. The condensers of the measuring apparatus were inter-calibrated.

3. The capacity of the dielectric container filled with air, C_{air}, was measured.

4. The contents of H were blown over into G. (The cork which closed G was provided with a channel to allow the displaced air to escape.)

5. The capacity of the dielectric container filled with the given dielectric, $C_{liq.}$, was measured.

The dielectric constant of the liquid was (subject to a correction to be discussed hereafter) given by the ratio $C_{liq.}/C_{air}$ (to the standard $\varepsilon_{air} = 1$).

The apparatus when first used gave results subject to a troublesome inconsistency. The value of the $D.C.$ of a liquid when measured with the full accuracy of the method differed from that measured in the manner described above. The reason for this inconsistency may also account for some of the grave irregularities which are evident on comparing the values of the dielectric constants determined by various workers. The $D.C.$ of a liquid is actually equal to the ratio $C_{liq.}/C_{air}$ only when the capacity of the dielectric container is due entirely to "replaceable" dielectric; *i.e.*, air or the liquid under examination. In practice, however, it is found impossible to eliminate entirely a small "residual" capacity due to that between the lead C and the earthed portions of the apparatus. This residual capacity is, in every measurement, added to that due to the liquid or air, respectively, and produces an error which increases with the $D.C.$ of the liquid. Thus the capacity due to the liquid is not the measured value, $C_{liq.}$, but a smaller value $(C_{liq.} - X)$, where X is the residual capacity. Similarly, the capacity due to the replaced air is not the measured value, C_{air},

but $(C_{air} - X)$. It is evident, therefore, that the true value of the *D.C.* is $(C_{liq.} - X)/(C_{air} - X)$. When, however, the dielectric container is itself of large capacity and of the form shown in the former paper (Fig. 2, J., *loc. cit.*), X becomes extremely small in proportion to the total capacity and may usually be disregarded. In the latter circumstances, the *D.C.* of a certain sample of ether was found to be 4·1140, but when measured in the condenser described above, the value of $C_{liq.}/C_{air}$ at the same temperature was 3·95. The replacement of the water in the thermostat by paraffin oil and the use of a glass instead of a metal vessel for containing the thermostatic liquid diminished the residual capacity considerably and increased the value of $C_{liq.}/C_{air}$ to $22394/5528 = 4·05$. Assuming that 4·1140 was the true *D.C.* of the ether sample, the value of X was taken as $\frac{\epsilon C_{air} - C_{liq.}}{\epsilon - 1}$* $= \frac{(4·1140 \times 5528) - 22394}{3·114}$ $= 105$ arbitrary units ($= 0·7$ micro-microfarad approx.). This value was applied as a correction to all the results here recorded. Each determination was performed in duplicate and no result was accepted unless the duplicate determinations were concordant.

Finally, the dielectric constants of a number of binary mixtures were examined in various proportions. For every determination shown in Table II sufficient of the two liquids to make 50 c.c. of the mixture was measured out from burettes.

Table I.

Dielectric Constants of Organic Liquids.

Temperature 25°. Frequency, $10^6 \sim$ per second (approx.).

	ϵ.		ϵ.
Benzene	2·23	Pentachloroethane	3·60
Toluene	2·33	Monochlorobenzene	5·44
Hexane	1·89	Dichlorobenzene	7·47
Ether (diethyl)	4·21	Ethylene dibromide	4·70
Carbon disulphide	2·58	*o*-Chlorophenol	6·31
Chloroform	4·79	Phenyl acetate	5·15
Bromoform	4·73	*iso*Butyl acetate	5·32
Carbon tetrachloride	2·20	Amyl acetate	4·62
Tetrachloroethane	7·83		

Results.

The dielectric constants of seventeen organic liquids, as measured by the above method, are recorded in Table I. The small but appreciable conductivity of a number of liquids, including the lower alcohols, acetates, oxalates, acetone, etc., prevented our

* $\epsilon = \frac{C_{liq.} - X}{C_{air} - X}$, $\epsilon C_{air} - \epsilon X = C_{liq.} - X$, $X = \frac{\epsilon C_{air} - C_{liq.}}{\epsilon - 1}$.

obtaining trustworthy measurements in such cases. It appears to us, however, that the dielectric constant of a substance containing an unknown number of free ions is, in any case, of little significance. Most of the liquids examined were of the B.D.H. "A.R." grade.

The results obtained for nine binary mixtures of organic liquids are set out in Table II and Fig. 2.

TABLE II.

Dielectric Constants of Binary Mixtures.

Temperature 25°. Frequency, 10^6 ~ per second (approx.).

Mixture.	Graph and mixture No.
A. Carbon tetrachloride. B. Ether (diethyl).	1
A. Chloroform. B. Ether (diethyl).	2
A. *o*-Chlorophenol. B. Ether (diethyl).	3
A. Carbon disulphide. B. Ether (diethyl).	4
A. Chloroform. B. Carbon disulphide.	5
A. Chloroform. B. Carbon tetrachloride.	6
A. *o*-Chlorophenol. B. Carbon disulphide.	7
A. Hexane. B. Carbon disulphide.	8
A. Ethylene dibromide. B. Hexane.	9

% A (by volume).	Mixture No. 1.	2.	3.	4.	5.	6.	7.	8.	9.
0	4·21	4·21	4·21	4·21	2·58	2·20	2·58	2·58	1·89
10	3·99	4·69	—	—	—	—	—	—	—
20	3·78	5·13	6·37	3·79	2·89	2·59	2·90	2·42	2·22
30	3·56	5·47	—	—	—	—	—	—	—
40	3·36	5·70	8·77	3·45	3·28	3·04	3·42	2·28	2·66
50	3·15	5·82	9·41	—	—	—	—	—	—
60	2·94	5·79	9·82	3·13	3·71	3·56	4·14	2·12	3·21
70	2·75	5·67	9·68	—	—	—	—	—	—
80	2·56	5·44	8·93	2·84	4·21	4·14	5·08	2·02	3·88
90	2·36	5·13	—	—	—	—	—	—	—
100	2·20	4·79	6·21	2·58	4·79	4·79	6·21	1·89	4·63

We desire to acknowledge a grant from the Department of Scientific and Industrial Research which enabled one of us (L. A. S.) to take part in this investigation.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, August 13th*, 1926.]

CCCXLV.—*Equilibrium in the Systems Nickel Sulphate–Potassium Sulphate–Water, Zinc Sulphate–Potassium Sulphate–Water, and Manganese Sulphate–Potassium Sulphate–Water at 25°.*

By Robert Martin Caven and William Johnston.

The experiments here described are a continuation of the work of Caven and Mitchell (J., 1924, **125**, 1428) to determine the limits of existence of double salts of the type $M^{II}SO_4,M^{I}_2SO_4,6H_2O$ in equilibrium with solutions containing their component salts, and to obtain evidence of the existence of the double salts in these solutions.

Lipscomb and Hulett (*J. Physical Chem.*, 1916, **20**, 75) have examined the system $ZnSO_4$–K_2SO_4–H_2O at 25°, and obtained results which differ from ours in showing potassium sulphate to cause a decrease in the solubility of zinc sulphate.

It has already been shown (*loc. cit.*) that the double salts $CuSO_4,M^{I}_2SO_4,6H_2O$(M^{I} = K or NH_4) are stable over wide ranges of temperature and relative concentrations of the component salts. Moreover, the continuous increase in solubility of each of the three simple salts caused by the addition of the second component up to the triple point, at which the double salt separates, was believed to indicate the presence of a considerable amount of the double salt, or its ions, in solution.

Experimental.

The Systems $NiSO_4$–K_2SO_4–H_2O *and* $ZnSO_4$–K_2SO_4–H_2O *at* 25°.

For the nickel system, solutions of the two salts were made at 40°, and various proportions of the two solutions placed successively in a flask, fitted with a stirrer, and kept in a thermostat at 25° ± 0·1°. The mixtures were stirred for 3 days, and then portions of the solutions and solid phases were separated and analysed.

The nickel was determined volumetrically by adding an excess of potassium cyanide and titrating back with standard nickel sulphate solution in presence of ammonia, diphenylglyoxime being used as indicator (Kelly and Conant, *Ind. Eng. Chem.*, 1916, **8**, 804). The potassium was calculated after determination of the total sulphate.

The procedure for the zinc system was the same as for the nickel system. The zinc was estimated volumetrically by the potassium ferrocyanide method, and the total sulphate determined.

The quantities in the tables are expressed as g. per 100 g. of solution (for the solutions) or of moist solid (for the "rests").

TABLE I.

The System $NiSO_4$–K_2SO_4–H_2O *at* 25°.

Solutions.			Rests.			
K_2SO_4.	$NiSO_4$.	H_2O.	K_2SO_4.	$NiSO_4$.	H_2O.	Solid phase.
10·59	Nil.	89·41	—	—	—	K_2SO_4.
11·16	0·33	88·51	39·63	14·59	45·78	K_2SO_4 and double salt.
4·93	1·35	93·72	25·00	20·75	54·25	Double salt.
4·15	3·90	91·95	24·35	21·85	53·80	
4·11	10·15	85·74	25·75	25·50	48·75	
4·75	15·66	79·59	32·50	31·32	36·18	
5·62	19·33	75·05	31·61	31·58	36·81	
6·82	23·09	70·09	32·22	32·76	35·02	
8·26	27·90	63·84	11·20	42·60	46·20	Double salt and $NiSO_4$,7H_2O.
6·30	27·92	65·78	1·45	48·75	49·80	$NiSO_4$,7H_2O.
3·82	27·87	68·31	0·55	50·32	49·13	
Nil.	27·94	72·06	—	—	—	

TABLE II.

The System $ZnSO_4$–K_2SO_4–H_2O *at* 25°.

Solutions.			Rests.			
K_2SO_4.	$ZnSO_4$.	H_2O.	K_2SO_4.	$ZnSO_4$.	H_2O.	Solid phase.
10·59	Nil.	89·41	—	—	—	K_2SO_4.
10·71	1·11	88·18	80·08	0·25	19·67	
10·94	1·91	87·15	43·35	26·00	30·65	K_2SO_4 and double salt.
6·52	4·73	88·75	32·09	29·37	38·54	Double salt.
5·99	5·40	88·61	31·04	28·69	40·27	
3·19	25·11	71·70	27·01	32·51	40·48	
2·27	33·08	64·65	26·08	35·21	38·71	
1·95	35·58	62·47	22·75	36·00	41·25	
1·82	36·00	62·18	25·51	36·23	38·26	
1·85	36·39	61·78	11·58	50·33	38·09	Double salt and $ZnSO_4$,7H_2O.
1·44	36·42	62·14	0·58	48·95	50·47	$ZnSO_4$,7H_2O.
Nil.	36·61	63·39	—	—	—	

The System $MnSO_4$–K_2SO_4–H_2O *at* 25°.

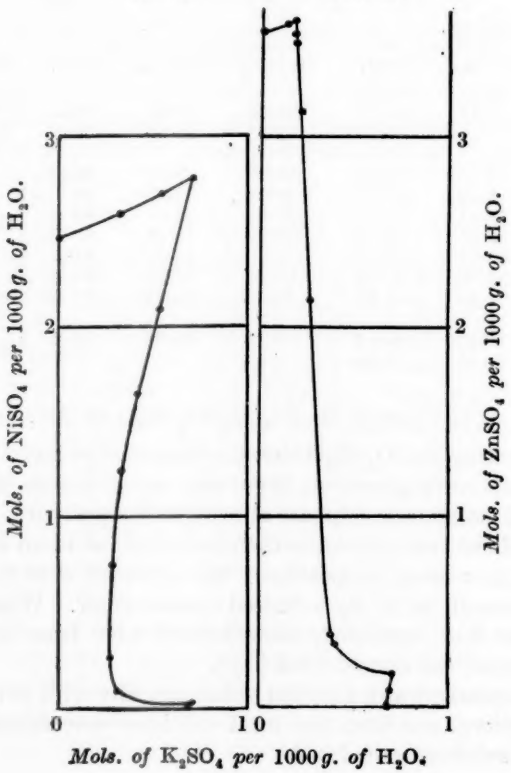
As the system $MnSO_4$–H_2O shows a transition point at 27°, whereafter the solubility decreases, there was no advantage in preparing solutions of manganese sulphate above this temperature. Saturated solutions of the two salts were therefore made at room temperature and mixed in various proportions; the mixtures were then evaporated isothermally at 25° by a filtered current of air. When sufficient solid phases had separated, the solutions were transferred to the reaction-vessel and stirred for 3 days.

The manganese was estimated volumetrically with permanganate by the Volhard method, the total sulphate determined, and the potassium sulphate calculated.

TABLE III.

Solutions.			Rests.			
K_2SO_4.	$MnSO_4$.	H_2O.	K_2SO_4.	$MnSO_4$.	H_2O.	Solid phase.
10·59	Nil.	89·41	—	—	—	K_2SO_4.
11·27	6·30	82·43	74·62	1·78	23·40	K_2SO_4.
12·04	15·22	72·74	77·46	3·66	18·98	K_2SO_4.
12·31	16·58	71·11	53·33	20·71	25·96	K_2SO_4 and double salt.
10·06	19·27	70·67	30·91	30·83	38·26	Double salt.
5·27	30·47	64·26	29·02	35·01	35·97	Double salt.
4·30	35·58	60·12	31·42	37·23	31·35	Double salt.
4·20	37·28	58·52	28·42	37·75	33·83	Double salt.
4·15	37·92	57·93	11·88	47·42	40·70	Double salt and $MnSO_4,4H_2O$.
3·03	38·21	58·76	1·25	56·66	42·09	$MnSO_4,4H_2O$.
2·46	38·42	59·12	0·83	58·42	41·75	$MnSO_4,4H_2O$.
1·87	38·54	59·59	0·66	57·35	42·99	$MnSO_4,4H_2O$.
0·43	39·03	60·55	0·17	60·01	39·82	$MnSO_4,4H_2O$.
Nil.	39·10	60·90	—	—	—	$MnSO_4,4H_2O$.

FIG. 1. FIG. 2.

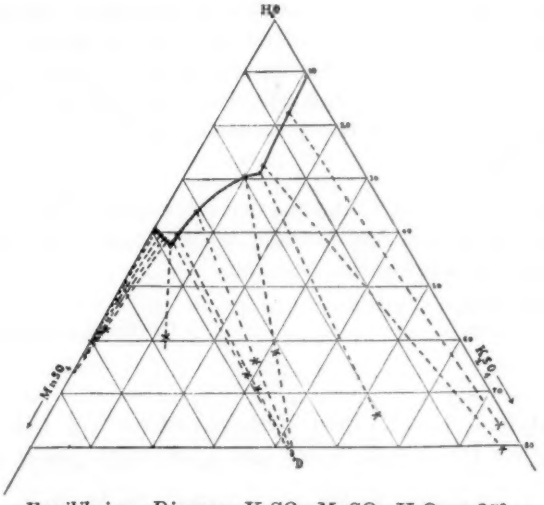


Conclusions.

1. Increase in solubility of potassium sulphate is observed when increasing quantities of nickel, zinc, or manganese sulphate are present, until the triple point is reached; and, reciprocally, increase in solubility of each of these three bivalent sulphates appears with increasing quantities of potassium sulphate up to the triple point in each case, although this increase is small with manganese sulphate.

These facts are shown for the nickel and zinc systems in Figs. 1 and 2, respectively, for which quantities are calculated, not as in

FIG. 3.



Equilibrium Diagram K_2SO_4–$MnSO_4$–H_2O *at* 25°.

The composition of the double salt is shown, by the co-ordinates of the point D *at which broken lines drawn through "rests" intersect, to be* $MnSO_4,K_2SO_4,4H_2O$.

the tables, where the percentage compositions of the solutions are shown with varying amounts of water, but as mols. of each salt per 1000 g. of water.

The manganese system is represented by a triangular diagram (Fig. 3), in order to show how the composition of the double salt is arrived at; but on this diagram, which corresponds with the figures in the table, the small increase in solubility of manganese sulphate does not appear.

2. The range of existence of each double salt at 25° is as follows:

Nickel potassium sulphate, from 0·031 to 3·8 mols. of $NiSO_4$ to 1 mol. of K_2SO_4.

Zinc potassium sulphate, from 0·19 to 21·3 mols. of $ZnSO_4$ to 1 mol. of K_2SO_4.

Manganese potassium sulphate, from 1·5 to 10·4 mols. of $MnSO_4$ to 1 mol. of K_2SO_4.

3. The relations between these concentrations in the case of the nickel double salt lead to a curious result which is seen when the figures are plotted on a rectangular diagram. Thus the double salt may be in equilibrium with the same concentration of potassium sulphate but with widely different concentrations of nickel sulphate; and the curve changes its direction so that its upper part is vertically above some of the lower part.

4. The shorter range in the case of the manganese double salt results chiefly from the large quantity of manganese sulphate which must be present before double salt formation can begin. This salt, however, cannot properly be compared with the others, because it has the composition $MnSO_4,K_2SO_4,4H_2O$, as indicated by Fig. 3. This result accords with the conclusions of Tutton (J., 1893, **63**, 342; 1896, **69**, 344).

The authors desire to thank the Governors of the Royal Technical College for a Research Assistantship which has enabled one of them (W. J.) to participate in this research.

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[*Received, July 27th*, 1926.]

CCCXLVI.—*An X-Ray Investigation of the Normal Saturated Dicarboxylic Acids and their Ethyl Esters.*

By ALEXANDER R. NORMAND, JOHN D. M. ROSS, and EDWARD HENDERSON.

A NUMBER of long-chain normal saturated dicarboxylic acids, $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$, and their ethyl esters have been prepared in this laboratory (Fairweather, *Proc. Roy. Soc. Edin.*, 1925, **45**, 283; 1926, **46**, 71) and it has been confirmed (Fairweather, *Phil. Mag.*, 1926, **1**, 944) that the melting points of the normal dicarboxylic acids containing an even number of carbon atoms lie on a curve which is approximately the mirror image of the corresponding curve for the acids having an odd number of carbon atoms. On the other hand, the melting points of the diethyl esters of the acids, both odd and even, lie on one curve.

In view of these results, it was decided to investigate the dicarboxylic acids and their ethyl esters by the *X*-ray method. It was thought that information might thus be obtained regarding the

structure of these compounds, and differences discovered between the structures of the " even " and the " odd " acids.

Several of the lower members of the series of dicarboxylic acids have already been examined by means of *X*-rays by Trillat (*Compt. rend.*, 1925, **180**, 1329). He finds that the largest spacings of a number of the even acids of this series, when plotted against the number of carbon atoms in the molecule, lie on a line which is parallel to, but not coincident with, the corresponding graph for the odd acids.

Two monoethyl esters of these acids have also been examined.

Experimental.

The procedure adopted was that used by Shearer and his co-workers. Thin layers of the substances were pressed or melted on glass plates and formed into narrow strips about 2 mm. wide and 1 cm. long. The glass plate with its layer of material was oscillated through a small angle on each side of the zero-position for times varying from 30 minutes to 3 hours, on a Müller *X*-ray spectrometer, in the path of a beam of *X*-rays (copper K_α radiation) from a Shearer *X*-ray tube run at about 30,000—50,000 volts.

Photographs were easily obtained from the monoethyl esters, but less readily from the diethyl esters. The lower members of the acid series gave good spectra, but those with a large number of carbon atoms gave only on long exposure the lines corresponding to the spacing associated with the length of the chain. In particular, the acid $CO_2H{\cdot}[CH_2]_{32}{\cdot}CO_2H$, although it readily gave lines corresponding to the spacings 4·1 and 3·7 Å.U. characteristic of many long-chain substances (compare Müller, J., 1923, **123**, 2043; Shearer, *ibid.*, p. 3152), gave very faint reflexions from the set of planes associated with the length of the chain.

In the series of the dicarboxylic acids the following results (in Å.U.) were obtained:

Acid.	M. p.	d_1.	d_2.	d_3.	d_4.	d_5.
$C_9H_{16}O_4$	107°	9·56	4·67	3·87	3·28	—
$C_{12}H_{22}O_4$	129	13·25	4·17	3·77	2·98	4·63
$C_{13}H_{24}O_4$	113·5	13·3	4·70	3·93	3·21	—
$C_{14}H_{26}O_4$	126·5	15·4	4·13	3·71	2·97	—
$C_{16}H_{30}O_4$	125	17·4	4·14	3·67	—	4·60
$C_{18}H_{34}O_4$	124	19·55	4·12	3·69	2·95	4·63
$C_{22}H_{42}O_4$	123·8	23·6	4·13	3·75	—	—
$C_{26}H_{50}O_4$	123·5	27·8	4·16	3·74	2·97	4·62
$C_{34}H_{66}O_4$	123	35·9	4·11	3·67	2·98	4·51

The following are the results given by Trillat (*loc. cit.*):

Acid.	M. p.	d_1.	Acid.	M. p.	d_1.
$C_4H_6O_4$	180 (185)°	4·5	$C_8H_{14}O_4$	140 (140)°	9·3
$C_6H_{10}O_4$	148 (153)	7·0	$C_9H_{16}O_4$	106 (107)	9·6
$C_7H_{12}O_4$	149 (103)	7·6	$C_{10}H_{18}O_4$	127 (133)	11·4

The figures in parentheses are the m. p.'s of the pure compounds as given by Fairweather.

An examination of these values shows that there is a considerable difference between the increment of d_1 in passing from an odd to an even acid (1·7—2·1 Å.U.) and that for the passage from an even to an odd acid (0·6—0·05 Å.U.).

In the above series, the average value of d_1 for the addition of two CH_2 groups is 2·1 Å.U. The measurements are in agreement with Müller and Shearer's conclusions as to the nature of the carbon chain in the fatty acid series (J., 1923, **123**, 3156), and the figures indicate that only one molecule lies between each pair of reflexion planes.

Regarding the difference in increment in d_1 in passing from an even to an odd acid and *vice versa*, Müller and Shearer (*ibid.*, p. 3161) suggested a type of carbon chain which, if placed with its direction of length normal to the long-spacing plane, would give rise to a difference between odd and even members of a series, the increments being of the same order as those given above. There is no *a priori* reason to assume that the molecules are arranged parallel to the normal to the reflecting plane; they may be inclined at any angle to it and the differences in the rates of increase in d_1 per CH_2 group observed from one series to another may be ascribed to a variation of this angle. This view receives direct experimental support from the measurements of single crystals of stearic acid by Müller (*Nature*, 1925, **116**, 45). He has shown that the crystal is monoclinic with a β angle of 120°, so that the *c* axis is inclined at 30° to the normal to the long-spacing plane (001). It is probable that the direction of length of the molecule coincides approximately with the *c* axis, so that it would make an angle of 30° with the normal to the plane.

With a zig-zag chain lying parallel to the normal, the addition of each CH_2 group would always result in the same increase of spacing; if the chain were tilted away from the normal, the even members would lie on one line and the odd members on an adjacent parallel line, and the increment in passing from an even to an odd acid would differ from that in passing from an odd to the next even acid—results which are in agreement with those actually found in both the fatty and the dicarboxylic acids.

As the series is ascended, the difference in d_1 between an even member and the next odd member diminishes, and thus the higher members of the series show little difference between an odd member and the even member immediately preceding it. This can be connected with the fact that the two melting-point curves of the odd and the even acids become asymptotic as the higher members of the series are reached.

The spacings d_2, d_3, d_4, and d_5 are much shorter than those associated with the length of the molecule. The spacings d_2 and d_3, which are about 4·1 and 3·7 Å.U., respectively, agree closely with those found by Müller and Shearer for the fatty acids and their esters, and are characteristic of many long-chain compounds. The two odd acids examined, *viz.*, the C_9 and the C_{13} acids, exhibit quite different values for the d_2, d_3, and d_4 spacings. The value given under d_2 agrees fairly well with the value for d_5 found for some of the even acids, and it may be that the line corresponding to the d_2 spacing is missing for the odd acids. If the spacings d_2, d_3, and d_4 are connected with the cross-section of the molecule, as is suggested elsewhere, it is clear that the structure of the odd acids differs materially from that of the even acids.

The lines corresponding to the spacings d_2 and d_3 appeared very readily in all cases, but in some cases those of the d_4 and d_5 spacings were not very distinct. In the lower members of the series the lines were well defined, but in the higher members the lines were more diffuse and so the degree of accuracy in measurement was diminished.

The crystal structure of succinic acid has been completely worked out by Yardley (*Proc. Roy. Soc.*, 1924, **105**, 451); the spacing found by her for the (010) plane, *viz.*, 4·46, is numerically equal to the value of d_1 found by Trillat for succinic acid. The spacings for the (011) and (101) planes, *viz.*, 4·71 and 3·69, respectively, are also approximately equal to the values for d_5 and d_3, respectively, found for the dibasic acid series.

In the series of the esters of the dicarboxylic acids the following results were obtained:

	M. p.	d_1.	d_2.	d_3.	d_4.	d_5.
$(CH_2)_{11}(CO_2Et)_2$	20°	22·7	—	—	—	4·63
$(CH_2)_{12}(CO_2Et)_2$	27	23·7	4·09	3·64	—	—
$(CH_2)_{14}(CO_2Et)_2$	43	28·5	4·08	3·56	—	—
$(CH_2)_{20}(CO_2Et)_2$	56	33·6	4·14	3·70	—	4·63
$(CH_2)_{28}(CO_2Et)_2$	74	43·7	4·10	3·69	—	4·53
$(CH_2)_{32}(CO_2Et)_2$	80	49·0	4·17	3·71	—	4·63

As mentioned above, the melting points of all these esters lie on one curve. The value given for d_1 for the first ester in the list is doubtful. Since the melting point was low (20°), the photograph was not a good one, and lines corresponding to spacings of 22·7 and 23·9 were obtained. It is our intention to investigate this ester again under more suitable conditions of temperature.

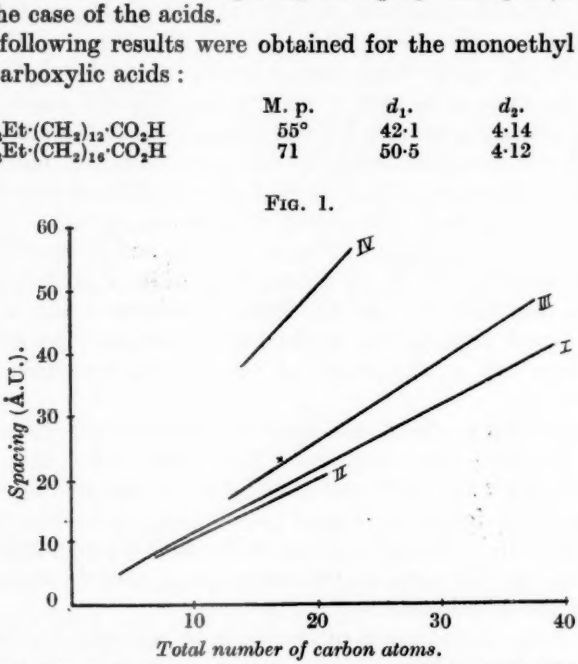
For the diethyl esters the increment in d_1 is 1·2—1·3 Å.U. per CH_2 group. These figures indicate that only one molecule lies between each set of reflexion planes. The increment in length for each carbon atom added to the chain is greater for the esters

than for the corresponding acids, and the structure is probably similar to that assigned by Müller and Shearer to the alcohols. The one odd ester examined fits into the same series as the even esters, and this is in agreement with the fact that the melting points all belong to one series. The spacings for d_2, d_3, and d_5 were the same as in the case of the acids.

The following results were obtained for the monoethyl esters of the dicarboxylic acids :

	M. p.	d_1.	d_2.	d_3.
$CO_2Et{\cdot}(CH_2)_{12}{\cdot}CO_2H$	55°	42·1	4·14	3·66
$CO_2Et{\cdot}(CH_2)_{16}{\cdot}CO_2H$	71	50·5	4·12	3·66

FIG. 1.



I *Dicarboxylic acids (even members).* II *Dicarboxylic acids (odd members).* III *Diethyl esters of the dicarboxylic acids (even members).* × *Diethyl ester of a dicarboxylic acid (odd member).* IV *Monoethyl esters of the dicarboxylic acids (even members).*

The odd-order reflexions from the d_1 planes were much stronger than the even-order reflexions. As was expected from the presence of a carboxyl group at one end of the molecule and an ethyl group at the other, the values obtained for d_1 are in agreement with the assumption that the reflexion planes associated with d_1 are separated by a distance approximating to twice the length of the molecule. The increment in d_1 per CH_2 group is 2·1 Å.U. or 1·05 Å.U. per molecule. This would indicate that the monoethyl esters have the same type of chain as the acids.

The figure shows the results plotted graphically along with those given by Trillat (*loc. cit.*). The actual rate of increase per CH_2 group in the dibasic acid series is very nearly the same as that found by Müller for the fatty acids, after allowing for the double layer in

the latter case, whilst the ethyl esters show a rate of increase similar to that of the corresponding esters of the fatty-acid series. It will also be noted that, for the dicarboxylic acids with a small number of carbon atoms in the chain, the graph departs from the straight line.

In view of the difficulty in obtaining good lines corresponding to the d_1 spacing in the case of the C_{34} acid, the following additional experiments were tried. Instead of pressing or melting the acid on a piece of glass, a large crystal of rock salt was used. When the acid was melted on, distinctly better photographs were obtained than when glass was used as the supporting medium. When the acid was merely pressed on, the results were no better than with glass. The polar character of the rock salt apparently caused more of the molecules to be oriented in the appropriate direction. When a fused silica plate was used in place of glass in the case of the C_{18} acid, the results were not quite so good as those obtained when glass was employed. An additional advantage in using rock salt is that its reference lines can be obtained on the same plate, thus facilitating the measurement of the plate.

Conclusions.

This investigation shows that the even and the odd members of the dicarboxylic acids belong to two distinct series. So far as the results go, the odd and the even members of the diethyl esters of these acids form one series. From the spacings observed, it is concluded that the monoethyl esters contain two molecules, whilst the other substances examined contain only one molecule between successive reflecting planes.

Our thanks are due to Messrs. Brunner Mond and Co. for a grant for the purchase of the *X*-ray spectrometer; to Sir James Walker for his suggestions and continued interest in the work; to Dr. D. A. W. Fairweather for providing the chemical substances; to Sir William Bragg for permission to study methods in use at the Davy Faraday Laboratory; and to Dr. G. Shearer for advice and helpful criticism.

UNIVERSITY OF EDINBURGH. [*Received, August 3rd,* 1926.]

CCCXLVII.—*Studies of Precipitated Solids. Part I. Strontium Sulphate.*

By BERTRAM LAMBERT and WILLIAM HUME-ROTHERY.

IN Gmelin and Kraut's "Lehrbuch der Chemie" it is stated that "strontium sulphate is formed as a white powdery precipitate by adding dilute sulphuric acid, or other sulphate, to a dilute solution

of a strontium salt . . . or, if concentrated solutions are used, as an amorphous, flocculent precipitate, becoming crystalline." No reference has been found to any detailed or systematic study of the effects of the conditions of precipitation upon the type, nature, and size of the precipitated particles of strontium sulphate. In the present work, the effects of variations in the concentration, temperature, cation, and anion of the precipitating solutions have been investigated within the following limits:

(*a*) Temperature of precipitation, from 0° to 100°.
(*b*) Concentration of solutions, from 0·01*N* to 3·47*N*.
(*c*) Cations of the sulphate solution, $H^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$.
(*d*) Anions of the strontium salt solution, Cl', NO_3', $CH_3{\cdot}CO_2'$.
(*e*) Times of exposure of precipitate to mother-liquor, from shortest possible time up to one week.

All the materials employed were very carefully purified and tested before use, and the concentrations of the solutions checked from time to time; the precipitations were carried out in carefully cleaned and steamed glass vessels; the temperatures of precipitation were controlled to within $\pm$ 1°, and great care was taken to prevent alterations in the concentration of the solutions—an important point when working at the higher temperatures.

Owing to the rapid changes undergone by the precipitate, when left in contact with the mother-liquor—in some cases 10 seconds' exposure caused profound alteration—a quick method of filtration had to be used: this was achieved by using "alundum" filtering cones and a rapid-acting filter-pump.

All precipitates were examined microscopically in ordinary and in polarised light, a microscope with a rotating stage being used for measurement of the angles of the crystals. The procedure adopted, and found very satisfactory, for mounting the precipitates prior to examination was as follows: A portion of the washed precipitate was transferred to a watch-glass and stirred with a little pure alcohol (this was definitely proved to have no action on the precipitate); a drop of this suspension was placed on a microscope slide and, after careful evaporation of the alcohol, a cover-glass was adjusted over the precipitate and effectively sealed round the edges with Canada balsam.

I. *Effects of Variations in the Concentration of the Solution, and in the Temperature of Precipitation, upon the Type of the Precipitated Particles.*

Equal volumes of equivalent solutions of strontium chloride and sulphuric acid were used throughout this section of the

work, the sulphate solution being added to the strontium salt solution in all cases. The results of more than 350 experiments may be summarised as follows :

(1) *Precipitates obtained with* 3·47N—0·35N-*Solutions.*—At all temperatures from 0° to 100° the *initial* precipitate produced was voluminous and flocculent in appearance, and occupied the whole volume of the solution. This bulky precipitate consisted of fine, needle-shaped crystals, usually too narrow for measurement and of a length dependent upon the conditions of precipitation (see p. 2643). On standing in contact with the mother-liquor, the bulky, flocculent form of precipitate was transformed into a fine, powdery form occupying a small volume and consisting of crystalline particles belonging to the rhombic system. For the present, these two types of precipitated strontium sulphate will be referred to as " needles " and " rhombs," respectively. The rate of change needle $\longrightarrow$rhomb was markedly increased by rise of temperature and, to a less extent, by the increase in the concentration of the mother-liquor (hydrochloric acid). At 100°, the change was complete in 10 seconds. The needle-shaped particles are illustrated ($\times$ 200) in Fig. 6.

(2) *Precipitates obtained with* 0·35N—0·125N-*Solutions.*—Between these concentrations the formation of needles was confined to limited ranges of temperature dependent upon the concentration. This may be illustrated by consideration of the results obtained with 0·25*N*-solutions. At 0°, the *initial* precipitate consisted entirely of rhombs and contained no needles; at 50°, slight flocculation was observed in the initial stages of precipitation and needles were found in the mounted precipitate; as the temperature of precipitation was raised, flocculation became more and more marked and a larger proportion of needles was found in the precipitate; at 85°, flocculation abruptly ceased and the initial precipitate formed between this temperature and 100° consisted entirely of rhombs.

Similar results, with different temperature limits, were obtained with 0·15, 0·2, and 0·3*N*-solutions, and it was thought that there might be a definite range of temperature within which a solution of given concentration would give both types of precipitate as the product of *initial* precipitation. Careful experiments showed, however, that this was not so: the upper temperature limit of needle formation altered considerably from time to time, and it was conclusively proved that identical solutions would yield different results in different laboratories owing, it is supposed, to the effect of nuclei of crystals in the air.*

* Compare Johnson, Mervin, and Williamson (*Amer. J. Sci.*, 1916, **41**, 473), who found that the transition temperature between the calcite and aragonite forms of precipitated calcium carbonate varied from time to time.

(3) *Precipitates obtained with Solutions of Concentration less than* 0·125N.—Under these conditions of concentration the precipitates produced at all temperatures between 0° and 100° consisted entirely of rhombic particles; there was a complete absence of flocculation and no needles were ever observed in the precipitate.

It appears, then, that two definite crystalline types of strontium sulphate are produced by direct precipitation—one consisting of rhombic and the other of needle-shaped particles; the latter type is unstable and undergoes transformation into the more stable rhombic type of particle at speeds dependent upon the concentration of the mother-liquor and, to a greater extent, upon the temperature. The formation of the unstable type of precipitate is confined to solutions of greater concentration than 0·125*N* and is always accompanied by flocculation. Flocculation is completely absent when the initial product of precipitation consists

FIG. 9.

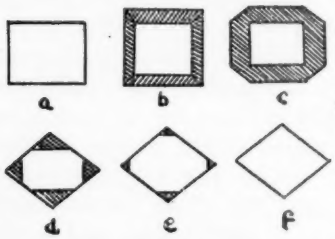
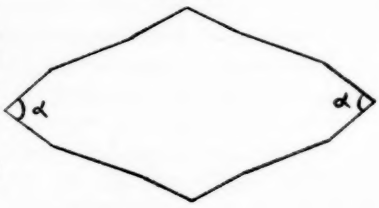


FIG. 10.



only of rhombic particles, and the particles produced under these conditions are remarkably regular in size. The rhombic particles formed by the transformation of needle-shaped particles are irregular in size and markedly larger except when formed at low temperatures. For instance, with 0·25*N*-solutions the rhombic particles produced by the initial precipitation above 90° were of average size 10 μ and maximum 11·5 μ; those formed by transformation of needle-shaped particles precipitated at about 80° were of average size 15 μ and maximum 25 μ.

The Nature of the Rhombic Particles.—The rhombic particles produced both by direct precipitation and indirectly from the needles varied greatly in form. Examination showed that these variations were not due to the production of essentially different crystalline particles, but to the gradual development of new faces on one and the same fundamental crystalline form, which belonged to the rhombic system and was identical with that of the mineral celestine.

Fig. 9 shows the effect of temperature on the shape of the rhombic

PLATE I

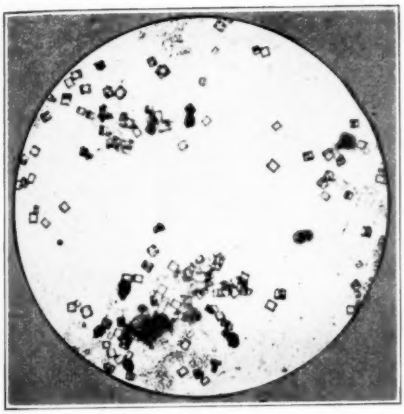


FIG. 1. × 200.

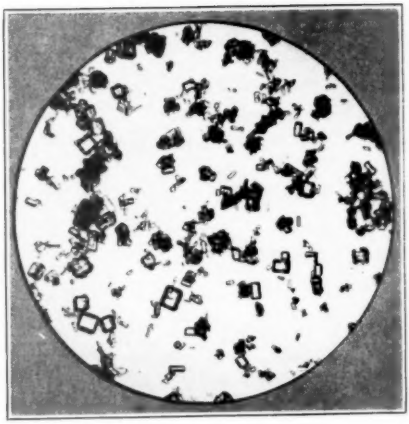


FIG. 2. × 200.

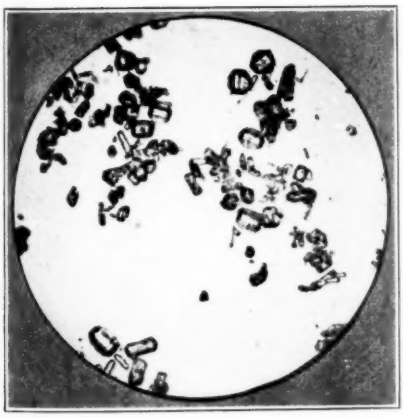


FIG. 3. × 200.

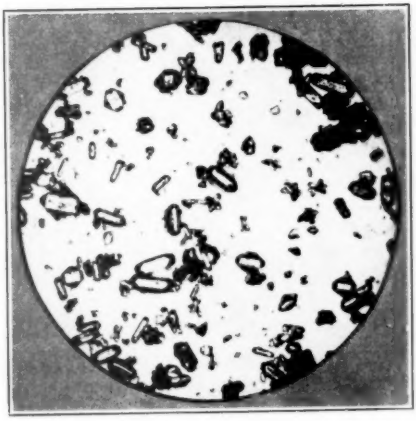


FIG. 4. × 200.

[*To face p.* 2640.]

PLATE II

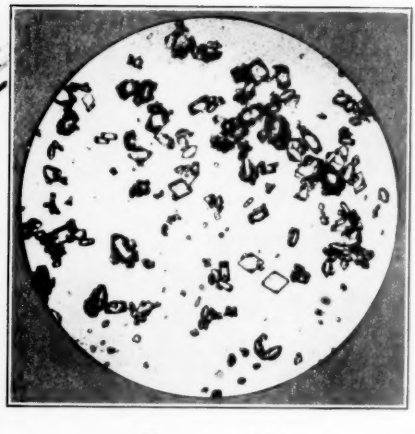


FIG. 5. × 200.

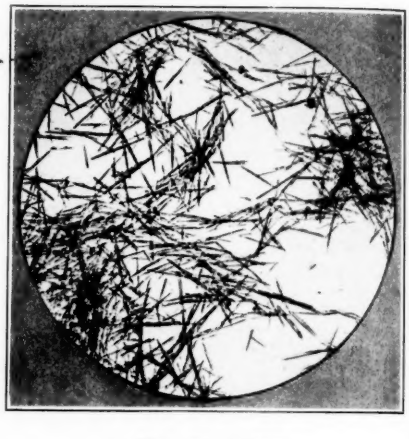


FIG. 6. × 200.

FIG. 7. × 200.

FIG. 8. × 200.

particles produced (indirectly from the needle variety) by precipitation with 3·47*N*-solutions of strontium chloride and sulphuric acid. At 0°, the particles were strictly rectangular in form, and when viewed through the microscope appeared as in Fig. 9*a*. On raising the temperature of precipitation, a new face began to make its appearance along the edges of the rectangular plate until, at 35°, the particles appeared as in Fig. 9*b*, in which the shaded portion is regarded as sloping downwards from the plane of the paper. At about 50° a new face began to appear along those edges of the plate perpendicular to the plane of the paper as shown in Fig. 9*c*. This face became more and more predominant as the temperature of precipitation was raised from 50° to 100°, the particles passing through the stages shown in Fig. 9*d*, *e*, and *f*, the pure rhombic form making its appearance at about 100°. This series of changes is shown for the 3·47*N*-solutions in Figs. 1 to 5, which represent the products of precipitation at 0°, 35°, 50°, 75°, and 100°, respectively.*

Alterations in concentration of the precipitating solutions also tended to produce a similar series of changes, increasing dilution favouring the production of the perfect rhombic form, but this effect was not so marked as that of temperature.

The rhombic crystals shown in Fig. 5 were identified with the celestine system by measurements of index of refraction (1·62—1·63), optical behaviour in polarised light, and measurements of their angles (75° ± 1° as compared with 75° 50′ for celestine). The 75° rhombs were also found to be anhydrous; in their various modifications, they were produced as the sole constituent of the final precipitate with solutions of strontium chloride and sulphuric acid of concentrations between the following limits: 0·01*N* to 0·05*N* at high temperatures, and 0·35*N* to 3·47*N* at all temperatures.

Between the limits 0·35*N* to 0·05*N*, however, a second series of rhombic particles made its appearance, having an angle 55° ± 1°, whilst in experiments with other cations and anions (see later) a third series, having an angle 43·5 ± 1°, was observed. These were all identified as further examples of the celestine series on the following grounds:

(1) Their index of refraction and optical properties agreed with those of celestine, and they were all anhydrous.

(2) If all three series belong to the same crystal system, a simple relation should exist between tan ½(75°), tan ½(55°), and tan ½(43·5°). The actual values are 0·767 : 0·520 : 0·399 or 3 : 2 : 1·5 approximately.

(3) In certain cases in which both 75° and 55° rhombs were

* These rhombic particles were of course formed indirectly from the needles, but the same effect was observed for the rhombs produced by direct precipitation in the more dilute solutions.

produced, a number of exceptionally interesting crystals were formed which appeared to be a "transition form" between the two types. The shape of the crystals is shown in Fig. 10, the angles denoted by α being approximately 75°, indicating the connexion with the celestine form. Fig. 7 contains three clear examples of these interesting crystals, which are rarely met with.

A corresponding transition form was found for the 43·5° rhombs and is shown in Fig. 8, the angle α again being approximately 75°.

These facts indicated that the 75°, 55°, and 43·5° rhombs all belonged to the celestine system, and this was confirmed by the fact that the 55° and 43·5° rhombs underwent the process of modification shown in Fig. 9. In these cases, the rectangular forms were not observed, but forms corresponding to Fig. 9*c*, *d*, *e*, and *f* were observed for the 43·5° and 55° rhombs just as with the 75° rhombs. On the other hand, some of the 55° rhombs, and particularly the modified 55° rhombs, became opaque after keeping for some time on the micro-slides, indicating that they were unstable. This fact was not satisfactorily accounted for, but it is possible that there were really two series of rhombs of approximately the same angle.

The Nature of the Needle-shaped Crystals.—The needle-shaped crystals were identified as a new hydrated form of strontium sulphate on the following grounds :

(1) They were more strongly doubly-refracting than the celestine rhombs.

(2) The index of refraction of the needles (estimated by observing their appearance when immersed in standard oils) was 1·55 approximately; the interference colours showed that the index of refraction in the direction of their length was greater than that at right angles to the length, but the exact values could not be determined.

(3) The needles were decomposed on keeping over sulphuric acid and also on exposure to air.

Attempts were made to analyse the needles, but these were unsuccessful because it was impossible to dry the specimen without causing some dehydration.

II. *Effects of Variation in* (1) *the Cation of the Sulphate Solution and* (2) *the Anion of the Strontium Salt Solution on the Type of the Precipitated Particles.*

Numerous experiments were carried out over ranges of concentration from 0·1 to 1·0*N* and over ranges of temperature from 0° to 100°. The following is a summary of the points established.

(1) Using solutions of the sulphates of sodium, magnesium, and

aluminium (to study the effects of uni-, bi-, and ter-valent cations), the strontium salt solution being the chloride :

(*a*) Needles (with flocculation) were produced at lower concentrations with sodium and magnesium sulphates than with sulphuric acid. Aluminium sulphate more closely resembled sulphuric acid.

(*b*) The limits of concentration and temperature within which the different types of rhombs appeared were different in each case, but no generalisations could be made. In all cases, however, the various types of rhombs underwent the transformation shown in Fig. 9—rise of temperature and decrease in concentration favouring the formation of the perfect rhombic particle : this appears to be a general rule for all the rhombic particles of strontium sulphate.

(2) Using solutions of strontium chloride, nitrate, or acetate, and sulphuric acid :

(*a*) Under comparable conditions of temperature and concentration the nitrate behaved, in general, like the chloride.

(*b*) With strontium acetate solution the formation of needles (with flocculation) took place in solutions as dilute as 0·1*N*. At 100°, rhombs alone were produced as the initial product of precipitation at all concentrations.

III. *Effects of Variations in Concentration, Temperature, Anion and Cation on the Size of the Precipitated Particles.*

Nearly 500 experiments were performed in this section, and the following summarises the conclusions which have been drawn, all remarks applying only to the particles of the initial precipitate and not to those formed by a secondary change.

(1) *Temperature Effects.*—(*a*) Under conditions when needles are formed, rise of temperature favours the production of longer and thicker needles, the effect being most marked at high concentrations. Thus, with 3·47*N*-solutions of strontium chloride and sulphuric acid the average needle length was 5, 5·5, 8, 13, and 15 μ at 0°, 25°, 50°, 75°, and 100°, respectively.

(*b*) Under conditions when rhombs are formed by direct precipitation, increase of temperature up to about 75° causes an increase in the size of the particle; but above 75° the effect is sometimes reversed. Thus with 0·1*N*-strontium nitrate and sulphuric acid solutions, the average size of the rhombs was 3, 6·5, 10, 11, and 7·5 μ at 0°, 25°, 50°, 75°, and 100°, respectively.

(2) *Concentration Effects.*—(*a*) Under conditions when needles are formed, increase of concentration causes the formation of a smaller needle, the effect being more pronounced at low than at high temperatures. Thus, at 0° the needle length was 15 μ and

5 μ for 0·5N- and 3·467N-solutions, but at 100° the lengths were 22 μ and 15 μ, respectively.

(*b*) Under conditions when rhombs are formed by direct precipitation, decreasing concentration leads to the formation of larger sized rhombs, but a limiting dilution is reached beyond which the effect is reversed. Thus at 100°, using 0·10, 0·05, 0·03, 0·025, 0·02, and 0·01N-solutions of strontium chloride, the sizes of the rhombs were 4, 6, 10, 8, 6, and 4 μ, respectively. As the temperature was lowered this limiting dilution moved towards higher concentration; thus, at 50° the maximum-sized rhomb was formed with 0·075N-solutions as compared with 0·03N at 100°.

(3) *Anion and Cation Effects.*—Under conditions when needles were formed, it was definitely established that the use of strontium acetate caused the formation of a much smaller needle than strontium nitrate or chloride under comparable conditions of temperature and concentration. A similar but much less pronounced effect was caused by substituting a metallic sulphate for sulphuric acid. The fact that three types of rhombs were produced makes it impossible to draw any definite conclusions about cation and anion effects when rhombs were formed.

IV. *The Effects of Variations in the Anion and Cation of the Precipitating Solutions on the Velocity of Precipitation.*

It was of interest, in connexion with the theory of precipitation, to study the effects of variation in the conditions of precipitation upon the time which elapses before the precipitate becomes visible, since strontium sulphate is one of the few substances suitable for such an examination.

A considerable number of experiments were carried out with 0·25N- and 0·10N-solutions. The results may be summarised as follows:

(1) *Cation Effects.*—Strontium chloride solutions were used and sulphates with the cations $H^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$. At 25°, 50°, 75°, and 100°, the times before appearance of the precipitate definitely increased with variations in the cations in the order $Na^{\cdot} < Mg^{\cdot\cdot} < Al^{\cdot\cdot\cdot} < H^{\cdot}$ when 0·25N-solutions were used. At 0°, the order was the same except that aluminium sulphate precipitated more slowly than sulphuric acid. With 0·10N-solutions, the order of increase in the times of appearance of the precipitate was the same at temperatures above 75°, but, at lower temperatures, $H^{\cdot}$ caused more rapid precipitation than any of the other cations.

(2) *Anion Effects.*—Sulphuric acid solutions were used and strontium salts with the anions Cl', NO_3', $CH_3{\cdot}CO_2'$. At all tem-

peratures the times before appearance of the precipitate definitely increased with variations in the anion in the order $CH_3{\cdot}CO_2' < Cl' < NO_3'$, using 0·25*N*-solutions. With 0·10*N*-solutions, the order of increase in the times of appearance of the precipitate was the same at temperatures above 50°, but was less definite below this temperature.

The theoretical significance of these results is discussed below.

Discussion.

The mechanism of precipitation of solids is very far from being a simple process, but it would seem that some light can be thrown on the subject by a consideration of the results obtained in this work. Von Weimarn (*Kolloid Z.*, 1909, **5**, 221) has shown that there is considerable evidence for the existence of an intermediate colloid stage in the formation of precipitates, and the results obtained from the study of the precipitates of strontium and calcium sulphates (the latter is considered in the following paper) afford strong support for this theory.

If von Weimarn's conception is valid, we may reasonably assume that the process of precipitation from solution takes place in the following stages: (1) Collisions of ions to form molecules of the insoluble substance; (2) aggregation of these molecules to form a disperse system (colloidal solution); (3) precipitation of the colloid (from sol to gel in some cases)—effected and affected by the remaining ions in the mother-liquor; (4) further aggregation of the colloid particles to form visible particles of solid; (5) changes of the solid particles owing to contact with the mother-liquor (formation of more stable forms, crystal growth, etc.).

The interpretation of experimental results will generally offer difficulties, since alteration in the conditions of precipitation may affect the velocity of any one or all of these stages. If, under a given set of conditions, any one of these stages is the predominant factor in the process of precipitation, the results obtained within such a range of experiment may throw some clear light on the subject. In this connexion, let us consider stage (3) of the process of precipitation.

It is known that barium sulphate forms a positively charged colloid (Kato, *Mem. Coll. Sci. and Eng. Kyōtō*, 1909—1910, **2**, 187; Feilman, *Trans. Faraday Soc.*, 1909, **4**, 176; Recoura, *Compt. rend.*, 1908, **146**, 1274) and it might reasonably be assumed that the analogous strontium sulphate, in the colloidal state, will have the same kind of charge. With a given anion, therefore, it is to be expected that the time taken for stage (3) of the precipitation will depend upon the protective power of the cation for a positive colloid.

In Section IV we have seen that, using 0·25*N*-solutions of strontium chloride and precipitating with equivalent solutions of sodium, magnesium, aluminium, and hydrogen sulphates (in this order) at temperatures from 25° to 100°, a definitely increasing time was required for the appearance of the precipitate. Now this same order—$Na^{\cdot} < Mg^{\cdot\cdot} < Al^{\cdot\cdot\cdot} < H^{\cdot}$—is the order of increasing protective power of these cations for a positive colloid. It would seem, then, that at this concentration and within this temperature range, stage (3) is the predominant factor in the precipitation.

Similar experiments with 0·10*N*-solutions gave the same order when precipitation was carried out above 75°, but, at lower temperatures, the hydrogen ion appeared to be less protective in its action than the other cations and it would seem that stage (3) had ceased to be the predominant factor. In this connexion, it may be noted that the viscosities of salt solutions are generally greater than those of equivalent solutions of their acids, and this may be the reason that sulphuric acid precipitated faster than metallic sulphates in these dilute solutions in which the particles have to travel a comparatively great distance.

When considering the precipitating effect of anions on positive colloids, we should expect $CH_3{\cdot}CO_2'$, because of the known abnormally high precipitating power of organic anions, to cause more rapid precipitation than Cl' or NO_3', and this is in agreement with our experiments. The order of the velocity of precipitation of strontium sulphate in the presence of the anions $CH_3{\cdot}CO_2'$, Cl', and NO_3' is the order in which these anions occur in the lyophile series. It is claimed that these results afford substantial evidence of the validity of von Weimarn's conception.

In the interpretation of the results of our experiments on the factors which influence the size of the precipitated particle, we are faced with some difficult problems. It has been definitely established that increasing dilution of the precipitating solutions leads to the production of a progressively larger solid particle until a critical dilution has been reached beyond which further dilution has precisely the opposite effect [see III, (2), (*b*)]. At first sight, it might appear that the effect of concentration was a simple result of the alteration in the velocity of precipitation, since rapid crystallisation is known to favour the formation of smaller crystals; but this simple conception is clearly not in accordance with the results obtained at great dilution. Further, increasing the temperature of precipitation undoubtedly increases the velocity of precipitation and should, on the same reasoning, lead to the formation of smaller particles; but there is no doubt that, in general, increasing tem-

perature tends towards the precipitation of a larger and not a smaller particle [see III, (1)].

Owing to surface energy effects the particles of a precipitate will tend to be as large as possible, but it is reasonable to suppose that there may be two main factors influencing their size: (*a*) Velocity of precipitation—increase of which favours a smaller precipitated particle; (*b*) facilities for diffusion—increase of which favours a larger particle. The facilities for diffusion must be connected with the viscosity of the solutions and particularly of the mother-liquor.

Increase of temperature will cause an increase in (*a*) and (*b*), but the predominating effect would seem, in most cases, to concern (*b*). Increase in the concentration of the precipitating solution results in more rapid precipitation without, apparently, any marked compensating effect on the facilities for diffusion, and leads to the formation of smaller particles [see III, (2), (*a*)]. The apparent anomaly at extreme dilution can be explained by assuming that there is a limiting dilution at which the decrease in (*b*) overcomes the effect due to slower precipitation, owing to the fact that the molecules will have to diffuse a comparatively long distance to form a larger particle. Since rise of temperature favours diffusion, we should expect the limiting concentrations to become more dilute as the temperature rises, in agreement with our results [see III, (2), (*b*)].

Variations in the anions and cations will clearly affect (*a*) and (*b*), but, in general, stage (3) of the precipitation, as affected by the influence of the anions and cations on the positive colloid, appears to predominate.

Summary.

The effect of conditions of precipitation upon the form and nature of the precipitated particles of strontium sulphate has been examined. It has been shown that under certain conditions the initial precipitate consists of fine needle-shaped crystals of a hitherto unknown hydrated form of strontium sulphate, to which, however, it has not been possible to assign a formula. On standing in contact with the mother-liquor, the needles are transformed into stable rhombic crystals of anhydrous strontium sulphate (celestine), which are also sometimes formed as the initial product of the precipitation.

The examination of the anhydrous rhombic particles has yielded interesting crystallographic information, a regular series of changes in form taking place with changes in the temperature and concentration of the precipitants.

Observations on the times which elapsed before the appearance of the precipitate when different salts were used have led to the

conclusion that the precipitation takes place through the medium of a colloidal form carrying a positive charge, the colloid being precipitated more or less rapidly according to the protective or precipitative effects of the other ions present. This conception accounts completely for the relative velocities of precipitation in the more concentrated solutions, but in dilute solutions other effects, such as viscosity, play an increasingly important part in determining the relative times of appearance of the precipitate.

The sizes of the particles produced by direct precipitation have been shown to depend on two main factors: (1) the velocity of precipitation, increase of which leads to a smaller particle, and (2) the facilities for rapid diffusion, which favour a larger particle.

Our thanks are due to Dr. T. V. Barker for his help and interest in the crystallographic part of this work, and we wish also to express our thanks to the Government Grant Committee of the Royal Society for a grant which covered part of the cost of the work.

UNIVERSITY MUSEUM, OXFORD. [*Received, July 17th*, 1926.]

CCCXLVIII.—*Studies of Precipitated Solids. Part II. Calcium Sulphate.*

By BERTRAM LAMBERT and ROBERT JOHN SCHAFFER.

TEXT-BOOKS on mineralogy describe a microchemical test for calcium involving the precipitation, under the microscope, of "radiating clusters of gypsum." Maschke and Vater (*Z. Kryst. Min.*, 1901, **33**, 57) investigated the form of the crystals which separated from saturated aqueous solutions of gypsum on evaporation at the ordinary temperature; they state that these crystals are prismatic in habit and usually simple in form, clusters being rarely formed and the crystals seldom twinned. Grengg (*Z. anorg. Chem.*, 1914, **90**, 327) described crystals of the hemihydrate $CaSO_4,\frac{1}{2}H_2O$ obtained by heating gypsum with various salt solutions. Copisarow (J., 1923, **123**, 796) described the formation of artificial alabaster by heating sodium sulphate and calcium chloride under pressure. He states that, in the precipitation of gypsum, no state of temporary supersaturation or gelatinisation could be observed, whereas, in the precipitation of calcium carbonate, a definite intermediate gelatinous form was seen. No reference has been found to any detailed or systematic study of the effects of the conditions of precipitation upon the type, nature, and size of the precipitated particles of calcium sulphate.

In this work, the effects of varying the conditions of precipitation have been investigated within the following limits :

(*a*) Temperature of precipitation, from 0° to 100°.
(*b*) Concentration of solutions, from 0·125*N* to 2*N*.
(*c*) Cations of the sulphate solutions, $H^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$.
(*d*) Anions of the calcium salt solution, $CH_3{\cdot}CO_2'$, Cl', NO_3', H_2PO_2'.
(*e*) Time of exposure of precipitate to mother-liquor, from shortest time possible up to 7 days.

All the calcium salts were prepared from a quantity of specially selected Iceland spar, these salts and all other materials used being very carefully purified. The method of experiment was substantially the same as that used in Part I (preceding paper). The results are conveniently described under three main headings.

I. *The Chemical Composition of the Precipitated Particles.*

Using equivalent quantities of any one pair of precipitants, it was possible (except in one case) to obtain precipitated calcium sulphate either in the form of the dihydrate ($CaSO_4,2H_2O$) or the hemihydrate ($CaSO_4,\frac{1}{2}H_2O$). Below a certain temperature the precipitate consisted of different forms of the monoclinic dihydrate, whilst, above this temperature, acicular crystals having straight extinction were produced; the latter were shown to be the hemihydrate. There was no evidence for the formation of a crystalline form of the dihydrate with straight extinction (compare Davis, *J. Soc. Chem. Ind.*, 1907, **26**, 726). It was definitely established that the stable phases above and below this temperature were the hemihydrate and dihydrate, respectively; the precipitate could be made to undergo the reversible change, $CaSO_4,2H_2O \rightleftharpoons CaSO_4,\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$, at this temperature, the change from hemihydrate to dihydrate being very rapid in comparison with the reverse change. This transition temperature was not, however, the same for different pairs of solutions, as is shown by Table I.

TABLE I.

Transition Temperature.

(Concentration 2*N*.)	Calcium acetate.	Calcium chloride.	Calcium nitrate.
Sulphuric acid	88°	96°	96°
Sodium sulphate	75	80	80

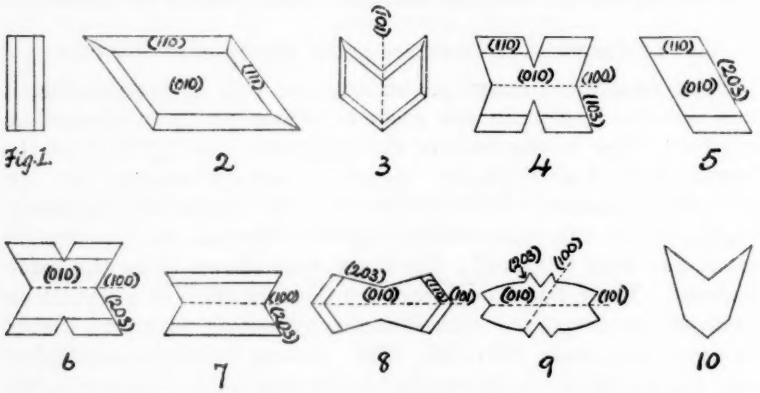
Precipitation with solutions of calcium nitrate and aluminium sulphate was unique in that crystals of the dihydrate were formed at all temperatures up to 100° and no crystals of the hemihydrate could be found in the product even after keeping at 103° for several

hours. Crystals of the dihydrate remained unchanged when heated with distilled water at 100° for several hours, although Davis (*loc. cit.*) claims to have brought about the transition in this way. In all the cases examined, with the exception of the above, the transition temperature lay between 75° and 96°.

Changes in the concentration of any given pair of precipitating solutions had little or no effect on the transition temperature; appreciable alterations in the transition point were produced only by changes in the nature of the precipitating solutions.

II. *The Crystalline Character and Size of the Precipitated Particles.*

(a) *The Hemihydrate.*—The hemihydrate was usually precipitated as acicular crystals having straight extinction. On standing in



contact with the mother-liquor, these developed sufficiently for their hexagonal form to be observed. With certain precipitants, *e.g.*, calcium acetate and sulphuric acid or sodium sulphate, the crystals were precipitated as hexagonal prisms similar to those produced by Grengg by heating gypsum with various salt solutions (Fig. 1). The length of the crystals varied considerably (8 μ—1000 μ), but no simple relation was found between their size and the conditions of precipitation.

(b) *The Dihydrate.*—Crystals of the dihydrate could be obtained by direct precipitation below the transition temperature or indirectly from the hemihydrate by precipitation above the transition point and subsequent cooling. The crystals obtained indirectly were always larger and more perfectly developed than those formed by direct precipitation. In either case they always occurred together in both simple and twinned forms [compare Maschke and Vater (*loc. cit.*)]. The size of the particles precipitated directly

under any given conditions varied between very wide limits (2μ to 100 μ), and this, together with the simultaneous formation of twinned crystals, made it impossible to trace any simple correlation between the conditions of precipitation and the average size of such particles: increase in the temperature of precipitation and decrease in the concentration of the precipitating solutions led—as appears usually to be the case—to an increase in the average size.

Again, no definite information could be obtained as to the factors influencing the relative numbers of simple and twinned crystals, but it was observed, qualitatively, that rapid precipitation [from reacting solutions of high concentration, or by using salts promoting rapid precipitation (p. 2653)] at the ordinary temperature favoured the formation of simple crystals, and slow precipitation the formation of twinned crystals. The governing factor cannot, however, be simply the velocity of precipitation, since increase in temperature (which increases the velocity of precipitation) favours the formation of twinned and not of simple crystals.

Maschke and Vater (*loc. cit.*) state that the "uninfluenced" form of simple gypsum crystals obtained by evaporation of aqueous solutions of calcium sulphate is (110)(010)(101). The simple crystals obtained by precipitation were not of this form: the faces (111)(1$\bar{1}$1) were developed and so the crystals have the form (110)(010)(111) (Fig. 2). The twinned crystals were also of the same form. As a rule, the twinned crystals formed by direct precipitation were of the "arrow-head" type, the twin plane being (101) (Fig. 3), but at temperatures immediately below the transition point similar twins on (100) were sometimes observed. Similarly, twinned crystals of the dihydrate formed indirectly were twinned either on (100) or on (101), twins on (100) occurring much more frequently when formed indirectly than when formed directly.

The simple crystals, whether formed directly or indirectly, were always prismatic in the direction (100) and variations in the temperature and concentration of the precipitating solutions had no effect on their habit; but the effect of similar variations on the habit of the twinned crystals was well marked. When precipitated from solutions of calcium chloride or nitrate by means of sulphuric acid at temperatures from 0° to 50°, the twinned crystals were either tabular or somewhat prismatic in the direction of the twin plane (101); at these lower temperatures, their habit was not affected by changes in the concentrations of the precipitating solutions. When precipitated from the same solutions at higher temperatures, the habit of the twinned crystals was definitely affected by the concentration of the precipitating solutions; the crystals were tabular in habit when precipitated from concentrated

solutions, but those precipitated from dilute solutions were prismatic in the direction of (100).

When twinned crystals were precipitated from calcium chloride or nitrate solutions by solutions of metallic sulphates, the twins were always tabular in habit.

The above remarks as to the form of the dihydrate crystals refer to precipitation in which the mother-liquor did not contain acetate ions; when this ion was present in any appreciable quantity, several new faces were developed on the crystals. In the presence of free acetic acid (*e.g.*, when equivalent quantities of calcium acetate and sulphuric acid were used), when the concentration of acetate ion was very small, the normal form (110)(010)(111) was precipitated. In the presence of greater quantities of acetate ion—whether added before the precipitation (by using excess of calcium acetate, or by introducing a soluble acetate into the precipitating solutions), or produced as a by-product of the reaction—new forms were obtained in which the faces (203) or (103) replaced (111)(1$\bar{1}$1). The face (103) is found in natural crystals of gypsum, but (203) has not hitherto been described.

The crystals precipitated in the presence of acetate ion were, therefore, either (110)(010)(103) or (110)(010)(203); the former were always produced as cruciform twins, twinned on (100) as shown in Fig. 4, whilst the latter frequently occurred as simple crystals prismatic in the direction of (100) or (203) as shown in Fig. 5, as well as in a variety of twinned crystals depicted in Figs. 6, 7, 8, and 9.

When calcium hypophosphite solutions were used, equivalent quantities of the precipitants gave the normal type of dihydrate crystals, but a large excess of the hypophosphite gave similar results to those given by a low concentration of the acetate (Fig. 9). Apart from these two salts, however, the form of the dihydrate crystals was not affected by excess of any one of the precipitants.

It would seem as though the acetate ion has the power of exerting an orienting force sufficiently strong to determine the form of the precipitated crystals of calcium sulphate. The possibility that intramolecular forces play some part in determining crystal form is now being recognised, and Tutton ("Crystallography and Practical Crystal Measurement," 1922, p. 1417) has suggested that such forces may ultimately be traced to the electrons—probably those in the outer ring.

A study of the effects of leaving the precipitated dihydrate particles in contact with the mother-liquor led to some interesting observations and conclusions about crystal growth. It was observed, qualitatively, that larger and more regularly developed crystals

generally resulted from such treatment, but no simple generalisation could be deduced as to how far this rate of growth depended upon the temperature, concentration, and composition of the mother-liquor.

Two interesting relevant points were (*a*) the development of solution faces and (*b*) the development of " arrow-head " twins.

(*a*) Whenever crystals were precipitated directly in a sufficiently developed state, the angle between (101) and (100) was clearly defined as a sharp point, but when the crystals were left in contact with the mother-liquor this sharp angle became rounded and, after a time, the faces ($\bar{1}11$)($1\bar{1}1$) were developed. In cases where the crystals under observation were too small for the pyramidal faces to be distinguished, the trace of ($\bar{1}01$) was observed and the presence of ($\bar{1}11$)($1\bar{1}1$) inferred by analogy with the larger crystals. This confirms the hypothesis that the rounded and water-worn faces ($\bar{1}11$)($1\bar{1}1$)—pyramidal faces on (101)—found on natural gypsum crystals are due to solvent action.

(*b*) The arrow-head twins were shown to be twinned on (101) and, since the simple crystals are holohedral, the edges of the twins should be parallel (Fig. 3). When first precipitated, this was not the case. Crystals of the form shown in Fig. 10 were produced, but on standing in contact with the mother-liquor the crystals grew until, ultimately, the edges were parallel. More than 250 measurements were made of the acute angle of the twinned crystals obtained at different temperatures and concentrations, both immediately after precipitation and after they had been left in contact with the mother-liquor for varying times. The figures obtained could be divided into five groups of 21°, 26°, 36°, 44°, and 52·5°, corresponding to the possible crystal faces (401), (301), (201), (302), and (101), respectively, the last being the normal face which was favoured by high temperature and low concentration of the precipitating solutions. A similar phenomenon was observed when simple crystals of sufficient size for measurement were precipitated at low temperatures. At high temperatures, the normal face was developed on the initial crystals.

We thus have a direct proof that gypsum crystals grow in stages, with the development of a possible crystal face at each stage, and that the generally accepted view that crystal growth takes place by the deposition of parallel layers is not always true.

III. *The Effect of Variations in the Anion and Cation of the Precipitating Solutions on the Velocity of Precipitation.*

The velocity of precipitation, measured by the time which elapsed between the mixing of the precipitants and the first visible appear-

ance of the precipitate, varied not only with the temperature and concentration of the solution, but also with the anion and cation of the precipitants. The latter variations are of interest as affording evidence of the existence of an intermediate colloidal form of calcium sulphate which is precipitated or protected by ions present in the mother-liquor. Tables II and III show typical results, the order of the velocity of precipitation being the same at other temperatures and concentrations examined.

TABLE II.

H_2SO_4 and	Temp.	2*N*.	1*N*.	*N*/2.	*N*/4.
$CaAc_2$.*	0°	20 secs.	30 secs.	135 secs.	—
	16	10 ,,	20 ,,	90 ,,	25 mins.
	50	2 ,,	5 ,,	20 ,,	3 ,,
	75	Immediate.	Immediate.	10 ,,	35 secs.
	100	,,	,,	3 ,,	5 ,,
$CaCl_2$.	0	45 secs.	4 mins.	—	—
	16	25 ,,	2·25 ,,	30 mins.	7—8 hours.
	50	10 ,,	60 secs.	3 ,,	20 mins.
	75	6 ,,	45 ,,	2 ,,	10 ,,
	100	5 ,,	30 ,,	1 ,,	7 ,,
$Ca(NO_3)_2$.	0	65 secs.	8 mins.	—	—
	16	40 ,,	5 ,,	45 mins.	7—8 hours.
	50	15 ,,	80 secs.	10 ,,	25 mins.
	75	10 ,,	60 ,,	6 ,,	10 ,,
	100	8 ,,	45 ,,	4 ,,	7·5 ,,

* In *N*/8-solutions the times for 16°, 50°, 75°, and 100° are 60, 7, and 4 mins. and 27 secs. respectively.

TABLE III.

(Temp. : 16°.)		Na_2SO_4.	$MgSO_4$.	$Al_2(SO_4)_3$.	H_2SO_4.
$CaAc_2$.	*N*/2	30 mins.	1 hour.	2 mins.	90 secs.
	1*N*	10 ,,	30 mins.	90 secs.	20 ,,
$CaCl_2$.	*N*/2	2·25 mins.	8 mins.	20 mins.	30 mins.
	1*N*	1·25 ,,	1·5 ,,	2 ,,	2·25 ,,
$Ca(NO_3)_2$.	*N*/2	5 mins.	20 mins.	25 mins.	45 mins.
	1*N*	2 ,,	4 ,,	5 ,,	5 ,,

As in the case of strontium sulphate, the effect of variation in the anion and cation of the precipitating solutions indicates that calcium sulphate forms a positive colloid. The anions $CH_3{\cdot}CO_2'$, Cl', and NO_3' caused a decrease, in this order, in the velocity of precipitation, and this is the order of the precipitating power of these ions for a positively charged colloid. With solutions of the nitrate and chloride of calcium, the cations $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $H^{\cdot}$ caused a decrease, in this order, in the velocity of precipitation, and this is the order of the increasing protective power of these cations for a positively charged colloid.

When calcium acetate solutions were used, the cation effect was not the same and the order of decreasing precipitating power was $H^{\cdot}$, $Al^{\cdot\cdot\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$. This is the order to be expected, since in

the case of $H^{\cdot}$ and $Al^{\cdot\cdot\cdot}$ the protecting ions are withdrawn as acetic acid and aluminium hydroxide respectively.

Summary.

1. From a given pair of precipitants, calcium sulphate can be precipitated directly either as the dihydrate or the hemihydrate. The determining condition is temperature and there is, for each pair of precipitants, a fairly definite transition point above which the hemihydrate and below which the dihydrate is stable.

2. The normal form of the precipitated dihydrate crystals is (110)(010)(111), which differs from the form (110)(010)(101) obtained by Maschke and Vater by crystallisation from aqueous solutions.

3. The presence of acetate ion has a marked effect on the form of the precipitated dihydrate crystals and gives rise to the forms (110)(010)(103) and (110)(010)(203), of which the latter has not hitherto been described. These forms have been observed to crystallise in a variety of twins, the type of twin being determined by the concentration of acetate ion.

4. Direct evidence has been obtained that the faces $(\bar{1}11)(1\bar{1}1)$—pyramidal faces on $(\bar{1}01)$—usually found rounded and water-worn on actual gypsum crystals owe their appearance to solvent action.

5. It has been shown that crystal growth does not always take place by deposition in parallel layers and that gypsum crystals grow in stages with the development of a possible crystal face at each stage.

6. The velocity of precipitation of calcium sulphate is affected by variations in the anions and cations of the precipitants in agreement with the hypothesis that it passes through a colloidal stage in which the colloid is protected or precipitated by the ions present in the mother-liquor.

We wish to express our thanks to Dr. T. V. Barker for valuable help and criticism and to the Royal Society for a grant which has covered part of the cost of this investigation.

UNIVERSITY MUSEUM, OXFORD. [*Received, July 17th*, 1926.]

CCCXLIX.—*The Influence of Intensive Drying on Inner Equilibria. Part II.*

By ANDREAS SMITS.

THE theory of allotropy assumes that every phase of the allotropic substance is composed of different molecular species which are in inner equilibrium when the behaviour of the system is unary, *i.e.*

when it behaves as a one-component system. In certain circumstances, the establishment of the inner equilibrium is very slow or even stopped and the substance then behaves as a poly-component system.

This theory enabled the author (*Z. physikal. Chem.*, 1922, **100**, 477) to give an explanation of the influence of intensive drying on the boiling points of nitrogen trioxide and nitrogen tetroxide as found by H. B. Baker and Mrs. Baker.

The view was that by intensive drying the inner transformations in a unary phase are stopped, *i.e.*, the inner equilibrium is fixed. In 1923, this phenomenon was discussed once more ("Theory of Allotropy," p. 316) in the light of Baker's new experiments (J., 1922, **121**, 568) and the original explanation was supplemented by

FIG. 1.

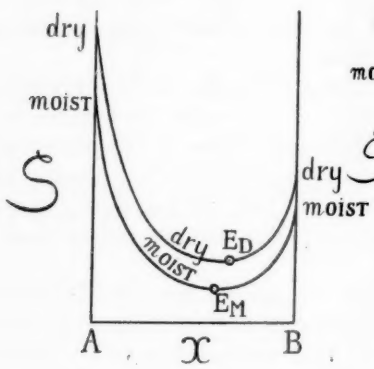
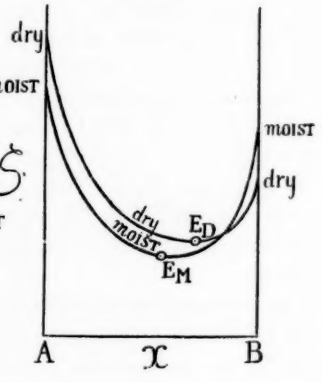


FIG. 2.



the assumption that the inner equilibrium is first displaced and then fixed (see also J., 1924, **125**, 1068).

Assuming that the so-called single substance exists in two molecular species α and β, three different cases may be considered :

A. It is possible that both α and β are more stable in the moist state than in the intensively dried state. In this case we obtain two curves for the values of the thermodynamic potential as a function of the composition x at constant pressure and temperature, one corresponding with the moist and the other with the intensively dried mixture. The curve for the more stable, moist mixture will have a lower value as indicated in Fig. 1. The inner equilibrium is always situated at the minimum point (see "Theory of Allotropy," p. 6), and from this graphical method we see clearly (1) that it would be quite fortuitous if the compositions of the dry and the moist inner equilibria were the same, and (2) that the composition

of the dry inner equilibrium may be situated either to the left or to the right of that of the moist inner equilibrium.

B. Another possibility is that α is stable in the moist and β in the intensely dry state. In this case we obtain Fig. 2, and the conclusions are the same as in the first case.

C. Finally, we have the possibility that the intensive drying has no influence at all on the stability of the pseudo-components. It is evident that in this case the ζ-x curves for the intensely dry and the moist mixtures coincide completely, and consequently the compositions of the dry and moist inner equilibria are also identical.

From these considerations, it follows that, if intensive drying has any influence on the stability of the pseudo-components, we may, in general, expect a displacement of the inner equilibrium by intensively drying a substance, but the direction of this displacement cannot be predicted. Thus the inner equilibrium may be shifted by intensive drying in one case in the direction of the more volatile pseudo-component α and in another case in that of the less volatile pseudo-component β. In the limiting case, this displacement may take place practically along the axis of one of the pseudo-components.

As regards the velocity with which inner equilibrium is established, the results obtained by H. B. Baker, Mrs. Baker, and myself show that the influence of intensive drying on the velocity of inner transformation may be very large; in several cases it appears that these inner transformations have ultimately stopped completely. In all probability this effect will not be so strong in every case, the final state depending on the individual properties of the substance, the state of aggregation, and the temperature.

THE UNIVERSITY, AMSTERDAM. [*Received, July 3rd,* 1926.]

CCCL.—*The Influence of Intensive Drying on Inner Equilibria. Part III.*

By ANDREAS SMITS, WILLEM DE LIEFDE, EMANUEL SWART, and ANTONY CLAASSEN.

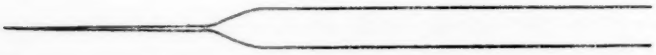
IN 1923 we began extensive investigations on intensive drying. Its influence on the boiling point of benzene was studied first: in agreement with the experiments of Baker, it was found that the boiling point of the intensively dried liquid was raised, and in agreement with experiments carried out by Smits in co-operation with Baker, it was observed that dried benzene behaved as a mixture (J., 1924, **125**, 1068).

These experiments did not settle whether this drying process was a fixation of the inner equilibrium, or whether it was a displacement of the inner equilibrium followed by fixation. As is shown in the "Theory of Allotropy," p. 320, the best way to answer this question is to study the influence of intensive drying on the vapour pressure, and since 1923 several pieces of apparatus for measuring vapour pressures have, therefore, been constructed in which different substances have been submitted to the process of intensive drying.

Since it was desirable to bring about intensive drying as rapidly as possible, the glass was first prepared. It is well known that any glass tubing contains extremely fine capillaries which may become filled with water during the cleaning process, and it requires a long treatment at high temperatures to remove the last traces of water.

To secure the removal of these capillaries each tube of high-melting Jena glass was first drawn out at one end (see Fig. 1), the capillaries at the sealed end being thus removed by fusion. The capillaries running along the wall of the tube are still open at the right-hand side, but all capillaries can be removed by slowly heating

FIG. 1.



the tube from left to right to such a temperature that fusion takes place. The tubes obtained in this way have a different appearance and are more brilliant than those which have not been so treated; they look more like quartz glass, which is also free from capillaries —quartz has also been used in some cases.

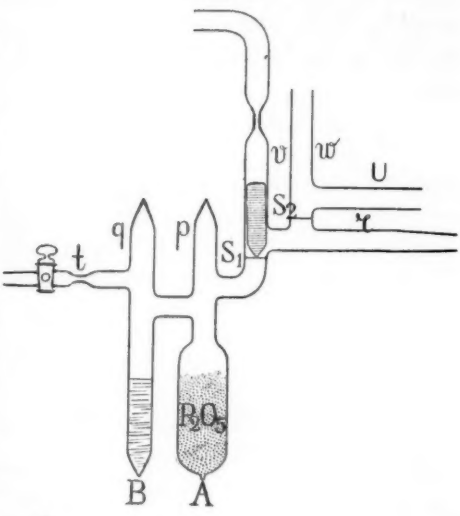
In our recent work all apparatus was constructed from high-melting Jena glass, freed from capillaries as described. The apparatus was then cleaned with a solution of potassium chromate and nitric acid, steamed, heated in a current of dry air, and finally evacuated, to test whether it was completely air-tight.

The removal of capillaries appeared to be extremely effective, since an apparatus with a volume of 2 litres could be evacuated within $\frac{1}{2}$ hour with the new Gaede steel mercury-vapour diffusion pump to such an extent that no discharge could be observed in the dark with a 3 cm. spark, even when the apparatus was heated to the melting point—a result which could never be obtained with glass not freed from capillaries.

The storage apparatus of capillary-free Jena glass, in which the substance to be studied was dried, is shown in Fig. 2. Before the vessel *B* was charged with this substance, phosphorus pentoxide had to be distilled into vessel *A*. Tube *p* was therefore sealed to the distilling tube, so that pure phosphorus pentoxide could be

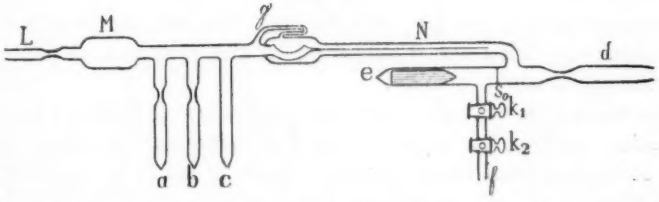
distilled in a current of dried oxygen, whilst tube *q* was sealed off and *t* was connected to a U-tube containing phosphorus pentoxide and a wash-bottle of sulphuric acid. Previous to this, the apparatus was dried in the way previously described (J., 1924, **125**, 2554). Pure phosphorus pentoxide was first distilled into vessel *A*, tube *q* opened, and vessel *B* filled with the substance to be studied, whilst a current of oxygen escaped by *q*, tube *t* being closed temporarily. After cooling *B* in a mixture of alcohol and solid carbon dioxide or in liquid air, *q* and *p* were sealed off successively and *t* was connected with the high-vacuum pump. When a high vacuum was reached, the capillary of tube *t* was sealed off. The substance in *B* was now distilled on to the phosphorus pentoxide in vessel *A*, and the storage apparatus was ready.

FIG. 2.



Two types of vapour-pressure apparatus were used, the first containing a glass-spring indicator and the second a mercury indicator. One of the first type is shown in Fig. 3. The newer patterns are made of capillary-free Jena glass with a glass-spring

FIG. 3.

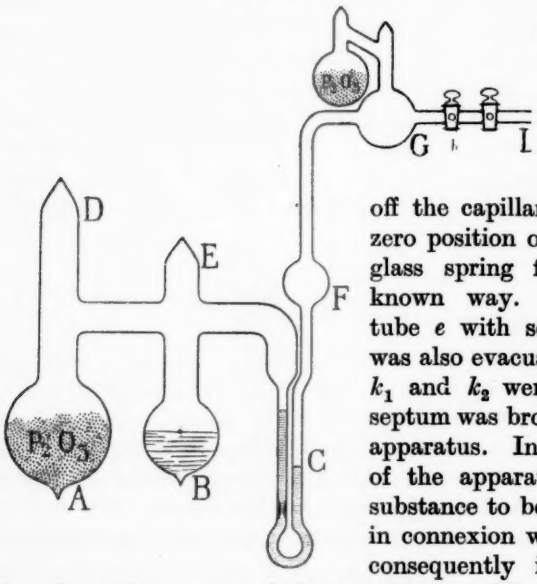


indicator substantially as described already (J., 1924, **125**, 2554). The apparatus was filled in the following way: Vessel *M* was sealed to the phosphorus pentoxide distilling tube, and tube *d* to tube *r* of the storage apparatus, which had been allowed to stand for some months. After heating the tubes, vessels, and breaker in a current of dried oxygen, the capillary ends of the tubes *a*, *b*, and *c* were

sealed off successively, and finally the oxygen left the apparatus by way of the breaker-tube v, connected to a U-tube with phosphorus pentoxide and a wash-bottle containing sulphuric acid.

Pure phosphorus pentoxide was now distilled into vessel M, L was sealed off, and tube v connected to the mercury-diffusion pump. When a high vacuum had been reached, v was sealed off. The septum S_1 was now broken by shaking the apparatus, and a small quantity of the previously-dried substance was distilled into tube c by cooling the latter. After sealing off tube d, the vapour-tension apparatus was set up rigidly, M cooled in liquid air, the connexion between the mantle of the glass spring and the vessel M broken by sealing off the capillary tube g, and the zero position of the needle of the glass spring fixed in the well-known way. Subsequently the tube e with septum S_0 (Fig. 3) was also evacuated, the two cocks k_1 and k_2 were closed, and the septum was broken by shaking the apparatus. In this way, that part of the apparatus containing the substance to be studied was never in connexion with the cocks, and consequently it was completely free from the vapour of the tap grease. After determinations of the vapour pressure at 20°, 30°, 40°, 50°, and 60°, the substance to be intensively dried was distilled on to the phosphorus pentoxide and the apparatus put aside.

FIG. 4.



The other type of vapour-pressure apparatus comprised a mercury indicator, such as has been used in this laboratory for many years. The construction of the apparatus, which is made of capillary-free Jena glass, is at once clear from Fig. 4, and it was filled as follows : Bulb A was filled with fine, distilled phosphorus pentoxide from a storage vessel and tube D sealed off while a strong current of dried nitrogen was passing through in the opposite direction. Bulb B was then filled in the same way with the substance to be studied and, after cooling this bulb, tube E was sealed off as short as possible. Subsequently bulb G was filled with about 10 c.c. of

pure dried mercury and sealed. Tube *L* was connected to the high-vacuum pump, whilst *B* was cooled in a bath of alcohol and solid carbon dioxide, or in liquid air, and bulb *A* was heated in a water-bath at 80°. In the meantime, the mercury was heated to drive out dissolved air. After closing cock *k*, the substance in bulb *B* was heated, to fusion if possible, and then cooled again. Cock *k* was then opened and the apparatus evacuated again. This process was repeated three times. Finally, cock *k* was closed again and the connexion to the high-vacuum pump broken. The tubes *C* were filled with mercury by inclining the apparatus, which was now ready. The mercury manometer is used here just as the glass spring is used in the first type and therefore we speak of a mercury indicator.

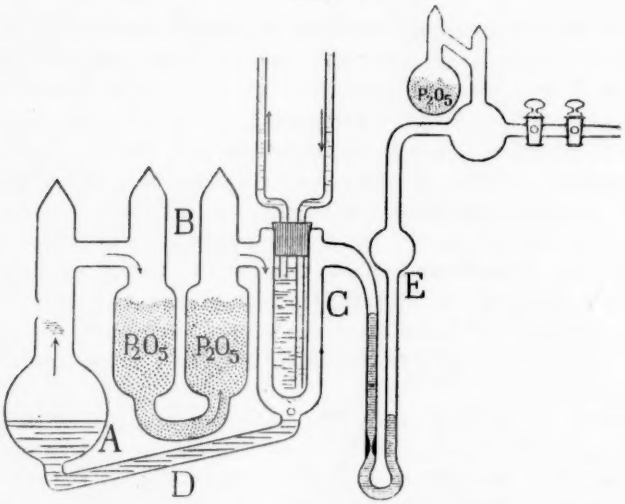
Wide tubes were considered very favourable for achieving rapid intensive drying, hence this last type of apparatus was made of tubes of 25 mm. internal diameter, and the quantity of phosphorus pentoxide was very large in proportion to the quantity of the substance to be dried. In our first investigations (1923), the quantity of phosphorus pentoxide was not so large and that is probably the reason why the experiments then made at 60° with a rather complicated apparatus containing a mercury indicator gave only negative results. At the time we thought this was due to the use of mercury and we continued our investigations with glass-spring indicators. Later, however, we found that the use of very pure dry mercury ought not to have an unfavourable influence, hence mercury was again used.

Since we wished to study the influence of distillation on the vapour pressure of intensively dried substances, it was necessary when using an apparatus of the first type (Fig. 3) that it should be provided with several tubes with capillaries. After a portion of the substance has been condensed in such a tube, the capillary can be sealed off and the vapour pressure determined again. The only difficulty here is that the process of intensive drying in an apparatus containing capillaries will require a much longer time than in an apparatus with very wide tubes.

With an apparatus of the second type (Fig. 4), capillaries are not necessary, for should it be desired to distil off a portion, it may be done quite easily in the following way. The pressure-difference between the left- and the right-hand side of the mercury indicator is raised to such a degree that the mercury is pressed up slowly into bulb *F* and vapour bubbles through it. When a sufficient quantity of the substance has been distilled off in this way, the mercury is passed back again into the U-tube *C* and the vapour pressure determined.

With the object of accelerating the drying process, we have modified the second type of apparatus in the way shown in Fig. 5. In this apparatus a circulation method is used especially for liquids. This circulation is caused by cooling the inner tube of the double-walled vessel *C* by means of a current of tap-water. Since the whole apparatus is placed in a bath at 45°, the vapour of the liquid is condensed on the outer wall of the inner tube of *C* and the condensed liquid drops into tube *D*, through which the liquid runs to the wide vessel *A*. Here the liquid is evaporated again, and after passing through the wide U-tubes, filled with very fine, pure phosphorus pentoxide, the vapour is again condensed in *C*, and so on.

FIG. 5.



This circulation is excellent; in an apparatus filled with 15 c.c. of benzene, 40 drops were formed per minute, so that the whole quantity in the vapour state passed through the U-tube containing phosphorus pentoxide about every 13 minutes—the rate may be regulated quite easily.

We have also constructed an apparatus which enables us to determine, not only the vapour tension of the residue, but also that of the distilled fraction. This apparatus, together with results obtained with carbon tetrachloride and benzene, will, however, be described in another paper. The present paper contains results obtained so far with nitrogen tetroxide and *n*-hexane with apparatus of the two types described. The vapour tensions of these dry, but not intensively dried, substances were determined in an apparatus of either type but without the bulb containing the phosphorus

pentoxide. The determinations were carried out at 20°, 30°, 40°, 50°, and 60°, so that the vapour-pressure curves of our preparations in the not-intensively dried state were known exactly.

In some experiments, the apparatus was placed in a bath at about 45°, and in others it was kept at room temperature, the intensive drying taking place at these temperatures. As is explained in the "Theory of Allotropy," it was very important to examine whether the vapour tension was changing *at these temperatures*, for, if this should be the case, a shifting of the inner equilibrium is proved. It is interesting also to determine the vapour pressures at intervals at higher temperatures, for, supposing the vapour pressure is not changed at the drying temperature, there is still the possibility that the inner equilibrium is fixed and that consequently the substance behaves as a mixture. If the temperature increases, a portion of the liquid evaporates and this brings about a change in the composition of the co-existing gaseous and liquid phases, which would correspond with a decrease in the vapour tension. That is the reason why the vapour pressure, although unchanged at the drying temperature, may show a decrease at higher temperatures.

At the same time, it follows that if the vapour pressure already decreases at the drying temperature, the decrease will become greater at higher temperatures. If, however, the vapour pressure increases at the drying temperature, this increase will become greater at slightly higher temperatures, but at still higher temperatures it will become smaller and may even change into a decrease.

Nitrogen Tetroxide.

We will first give the results obtained on drying nitrogen tetroxide, using three pieces of apparatus of the first type containing glass-spring indicators. The intensive drying here took place at room temperature. The nitrogen tetroxide had been prepared by Scheffer and Treub (*Z. physikal. Chem.*, 1912, **80**, 300) and the vapour-pressure curve as determined by these investigators was confirmed completely by our determinations. The phosphorus pentoxide was *completely* free from lower oxides.

Apparatus I (*not capillary-free glass*).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	17·70°	64·9	64·8	+0·1
20 months	20·00	72·9	72·0	+0·9*
24 „	20·38	75·1	73·35	+1·7

* After 20 months there was liquid in the capillary tubes. These tubes were now turned upward and the liquid was run into the bulb with phosphorus pentoxide.

Apparatus II (*not capillary-free glass*).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
½ month	22·00°	78·6	78·9	−0·3
3½ months	17·20	63·55	63·0	+0·5
20 ,,	19·80	72·4	71·2	+1·2
23 ,,	20·65	76·00	74·1	+1·9

On the day the last measurements were made we determined, with the same apparatus, vapour pressures at temperatures above the drying temperature, with the following results :

23 months	25·00°	92·95	90·6	+2·3
,, ,,	30·05	114·95	113·0	+1·9

As was expected, as the temperature rose the pressure increase passed through a maximum.

A quarter of the liquid was now distilled off into one of the tubes, and after sealing this off the vapour pressure was determined again at the drying temperature, with the following result :

23 months	20·65°	74·65	74·2	+0·4

Hence by distilling off a portion, the increase in the vapour pressure was diminished at 20·65° from +1·9 cm. to +0·4 cm. Eleven days later, the vapour pressure was again observed :

23¼ months	22·20°	81·07	79·60	+1·47

Thus the vapour pressure after 11 days had nearly re-attained its value before distillation.

The experiment was now repeated and a portion distilled off again :

23¼ months	22·20°	79·60	79·60	0·00

Again a decrease of the vapour pressure was observed, and it had become identical with the vapour pressure of the moist liquid at the same temperature. The following day, however, an increase of 0·5 cm. was again observed. It is proposed to study the change of the vapour pressure with the time after distillation with another apparatus filled with a larger quantity of nitrogen tetroxide. It should then be possible to change the increase into a decrease.

The results mentioned above show that the dried liquid behaves as a mixture, as though the inner equilibrium were not yet fixed. There is still a slow transformation in the direction of a new inner equilibrium, the position of which seems to be determined by the degree of dryness. The drying effect has not yet reached its maximum value in either of the two pieces of apparatus considered here; this can be proved by the results obtained with the third apparatus made of *capillary-free* Jena glass, which gave a larger

and still increasing effect in half the time, as is shown in the following table. Undoubtedly this rapid drying is to be ascribed to the use of capillary-free glass.

Apparatus III (*capillary-free glass*).

Duration of drying at room temp.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	19·80°	72·1	72·2	−0·1
10 months	18·20	67·8	66·0	+1·8
10½ ,,	19·75	73·1	70·8	+2·3
11 ,,	19·55	73·0	70·3	+2·7
16 ,,	22·90	85·4	82·1	+3·3

This series of experiments shows a much more pronounced rise of vapour tension, which will probably reach a much higher value after a longer interval has elapsed. Therefore the distillation experiments were not repeated here; the vapour-pressure measurements at higher temperatures had been made after 13½ months:

13½ months	20·75°	77·59	74·4	+3·2
,, ,,	25·23	95·33	90·9	+4·4
,, ,,	29·55	113·20	110·8	+2·4

Again, it is seen that on raising the temperature above the temperature of intensive drying the increase of the vapour pressure passed through a maximum.

Colour of the Intensively Dried Liquid.

Finally, we have studied the influence of intensive drying on the colour of the liquid. Two pieces of apparatus, each containing an observation tube of exactly 5 mm. diameter, were filled with nitrogen tetroxide, but one contained purest distilled phosphorus pentoxide also. After 22 months equal quantities of tetroxide were condensed in the observation tubes of each piece of apparatus and the colour of the liquid columns was compared at the drying temperature. The dried liquid had become darker brownish-red than the moist liquid. It is clear that the changes of both the vapour pressure and the colour at the drying temperature prove that the drying process brings about a shift of the inner equilibrium in the direction $N_2O_4 \rightarrow 2NO_2$, *i.e.*, in the direction of an endothermic reaction.

It is of interest to notice that, whilst we find that the vapour pressure of nitrogen tetroxide is increased by the process of intensive drying, H. B. Baker and Mrs. Baker (J., 1912, **101**, 2239) found that the boiling point of the intensively dried liquid had risen more than 47°. This seems to be contradictory, but it is not really so. When the boiling point is determined in the way given by H. B.

Baker and Mrs. Baker, a certain amount of liquid evaporates before the boiling point is reached. Now it is evident that, although the inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is shifted to the right-hand side, *i.e.*, the side of the more volatile pseudo-component, by intensive drying, which causes an increase in the vapour tension, a rise of the boiling point may nevertheless be observed, for, before the boiling point is reached, the liquid is partly evaporated, and while the inner transformations have become exceedingly slow, or have stopped completely, this evaporation will cause a change in the composition of the liquid, so that the vapour pressure, which showed an increase at first, now shows a decrease, corresponding with a rise of boiling point.

As Baker himself mentioned, it was not the true boiling point of the tetroxide which was observed: the liquid evaporated before the boiling point was reached and the thermometer recorded a temperature 47° above the boiling point. If the boiling point had been observed with the intensively dried liquid boiling under a reflux condenser while the volume of the vapour was kept very small, a *fall* in the boiling point should have been found, assuming the absence of superheating.

So we see that, as pointed out in "The Theory of Allotropy," p. 320, the determination of the vapour pressure is to be preferred for studying the process of intensive drying.

n-*Hexane*.

Among the substances which we have intensively dried at about 40°, none gave distinct effects as rapidly as hexane, although other substances behaved qualitatively in the same way, and the results with this compound are therefore given now:

Apparatus II (*of capillary-free glass*).

Duration of drying at *ca.* 40°.	Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
0	42·20°	30·80	31·00	−0·20*
4 weeks	42·10	30·45	30·90	−0·45
7 ,,	42·20	30·48	31·00	−0·52
10 ,,	40·15	28·05	28·70	−0·65
14 ,,	46·13	34·90	35·80	−0·90

* The liquid used was previously kept in a bottle with phosphorus pentoxide. We found that already this preliminary drying had caused a decrease of the vapour pressure of about 0·2 cm.

In contrast with what is observed with nitrogen tetroxide, the process of intensive drying brings about a decrease of the vapour pressure. Consequently, in this case the inner equilibrium is shifted in the direction of the less volatile pseudo-component.

As mentioned above, it was to be expected in these circumstances that, for temperatures above the drying temperature, the lowering of the vapour pressure relative to that of not-intensively dried hexane would increase. We carried out these experiments at the moment the decrease of the vapour pressure at about 42° was −0·52 cm. The following table shows the results:

Temp. of observation.	Pressure of dried liquid (cm. Hg).	Pressure of moist liquid (cm. Hg).	Drying effect (cm. Hg).
42·20°	30·48	31·00	−0·52
50·76	41·75	42·30	−0·55
61·20	59·42	60·20	−0·78

After distilling off a portion, the vapour pressure was as follows:

42·8°	20·60	31·60	−11·00

i.e., a very large decrease of the vapour pressure was found. This low vapour pressure, however, was not constant but rose slowly, so that after 2·5 hours the decrease was again about 1 cm.

Though the apparatus was in a thermostat, it was possible that, the liquid being partly distilled off, the temperature decreased. The following experiment was therefore carried out. The apparatus was taken out of the thermostat and placed on the table; after 2 hours, it had cooled to room temperature (the vapour pressure being 15 cm.) and was again placed in the thermostat, the rise of the vapour pressure with time being noted. The vapour pressure rose *very rapidly*, and the curve obtained in this way showed a very great difference from that obtained after distillation. It was thus proved that the slow rise of the vapour pressure after distillation was due to a slow inner transformation. From this we conclude that the inner equilibrium was not yet fixed, but the inner transformations were already very slow.

The original form of the explanation given by Smits (*Z. physikal. Chem.*, 1922, **100**, 477) of the observations made by H. B. Baker and Mrs. Baker (J., 1912, **101**, 2339) was that by intensive drying the inner transformations in a unary phase are stopped, the inner equilibrium is fixed, and a mixture is obtained which on distillation will, in general, give a distillate with a lower boiling point (higher vapour pressure) and a residue with a higher boiling point (lower vapour pressure) than the original liquid. It was concluded that the boiling points observed by Baker were abnormally high because the liquid mixture before reaching the boiling point had already partly evaporated.

Subsequent to the Bakers' later investigations (J., 1922, **121**, 568; 1924, **125**, 1068) Smits supplemented the original form of his explanation by the assumption that in the drying process the inner equilibrium can be displaced and *then* fixed. The experiments now

described with nitrogen tetroxide and hexane have proved that in these two cases the drying process effects a displacement of the inner equilibrium, and these two examples are contrasts, since in the case of nitrogen tetroxide the inner equilibrium is shifted in the direction of the more volatile, and in the case of hexane in the direction of the less volatile pseudo-component. Smits has indicated these two possibilities (see preceding paper).

From the fact that the effect obtained by partial distillation is followed by a return to the value before the distillation, it follows that the shifted inner equilibrium is not yet fixed.

It should be noted that Mali (*Z. anorg. Chem.*, 1925, **149**, 155) has studied the alteration of vapour pressure caused by drying carbon tetrachloride, benzene, and carbon disulphide for 5 months at 28° and also for 5 months at 44°. Since Mali did not record the vapour pressures of his moist preparations at different temperatures, it is safest to regard the vapour pressures of the preparations dried at 28° as corresponding with those of the moist substances; these preparations are hereafter, for the purpose of discussion only, referred to as the moist substances. The vapour pressures after 5 months' drying at 44° gave the following results on comparison with those of the moist substances, both kinds being at 44° :

Substances dried 5 months at 44°.	Drying effect at 44° (cm. Hg).
Carbon tetrachloride	−3·3
Benzene	−0·9
Carbon disulphide	−1·6

Hence Mali found very distinct decreases in the vapour pressures *at the drying temperature* after 5 months' drying at 44°. He did not emphasise the fact that only the results obtained at the drying temperature can throw light upon what happens in the drying process, but his conclusions are correct nevertheless.

Mali's experiments prove that the process of intensive drying produces a displacement of the inner equilibrium—in the direction of the less volatile pseudo-component in this instance. He did not distil the dried liquid but determined the vapour pressures at different temperatures. If we plot these vapour pressures against the temperature we see that the " moist " and " dry " curves at first diverge but subsequently converge at higher temperatures. The first effect is caused, as mentioned already, by the evaporation of the liquid, and the second is due, as we have found, to the fact that the mercury in the manometer is drying very slowly, so that, during the first period, the heating of the mercury causes a decrease in the degree of dryness. We found, on repeating the experiment after some weeks of intensive drying, that this effect of the mercury had diminished or vanished.

Mali's experiments show very distinctly, in agreement with ours, that intensive drying takes place more rapidly at 44° than at 28°.

Our next paper will deal with results obtained with other substances.

Summary.

In order to bring about intensive drying as rapidly as possible the glass was prepared by freeing it from its capillaries, and in the later experiments the apparatus was of high-melting Jena glass treated in this way.

Two types of vapour-pressure apparatus have been used: one with a glass-spring indicator and condensing tubes, and the other with a mercury indicator; in both cases the liquid from the storage vessel was distilled in the apparatus to effect intensive drying by purest distilled phosphorus pentoxide.

The second type of apparatus was made of wide tubes (25 mm. internal diameter) and the quantity of phosphorus pentoxide was relatively large, both these factors facilitating rapid intensive drying. An apparatus in which drying is expedited by a circulatory system is also described.

Some substances were dried at the ordinary temperature and some at about 45°. It was important to ascertain whether the vapour pressure was changing at the drying temperature, for, if so, a displacement of the inner equilibrium is proved (see "Theory of Allotropy").

The results are given of intensively drying nitrogen tetroxide at the ordinary temperature in an apparatus of the first type but with glass which had not been freed from capillaries: After 23 months' drying, the vapour pressure had risen 1·9 cm. Hg; a part of the liquid was distilled off and the increase in vapour pressure then fell to 0·4 cm., but after a further 11 days this had risen to 1·47 cm., *i.e.*, it had nearly regained its value before distillation.

In another apparatus, probably owing to the capillary-free glass, a greater drying effect was achieved in about half the time—after 16 months the vapour pressure had increased by 3·3 cm. On raising the temperature above that of the intensive drying, the increase of vapour pressure passed through a maximum, as had been anticipated on theoretical grounds.

The colour of the intensively dried liquid was a deeper brownish red than that of the "moist" liquid.

The changes of both the vapour pressure and the colour prove that the drying process had effected a displacement of the internal equilibrium in the direction $N_2O_4 \longrightarrow 2NO_2$.

The observation of H. B. Baker and Mrs. Baker that the boiling

point of the intensively dried liquid had risen more than 30° can be explained by the fact that a certain amount of the liquid had evaporated before the boiling point was reached.

The second substance dealt with is hexane. In contrast with the case of nitrogen tetroxide, the intensive drying here effects a decrease of vapour pressure. Other substances give similar but less pronounced effects. After only 14 weeks the decrease of vapour pressure had reached 0·9 cm., showing that the internal equilibrium is here displaced in the direction of the less volatile pseudo-component. The decrease of vapour pressure was augmented by raising the temperature above that of the drying, and a strong effect was obtained by distilling off a portion of the liquid at the drying temperature, as was expected.

After distillation the vapour pressure tends to revert to that before distillation, and this fact indicates that the displaced inner equilibrium is not yet fixed.

THE UNIVERSITY, AMSTERDAM. [*Received, July 3rd,* 1926.]

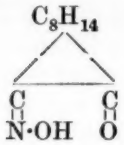
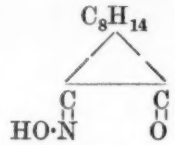
CCCLI.—*Studies in the Camphane Series. Part XLI. The Unstable Modification of* iso*Nitrosocamphor.*

By MARTIN ONSLOW FORSTER and KESHAVIAH ASWATH NARAIN RAO.

ALTHOUGH the existence of a low-melting, unstable *iso*nitroso-derivative in the product of the action of sodium and amyl nitrite on camphor has long been established (J., 1903, **83**, 534), the substance has remained obscure because the method of obtaining it is inconvenient. This consists in hydrolysing under strictly defined conditions the yellow *m*-nitrobenzoyl derivative produced in association with a colourless isomeride when *m*-nitrobenzoyl chloride acts on the Claisen mixture of *iso*nitrosocamphors (J., 1904, **85**, 904).

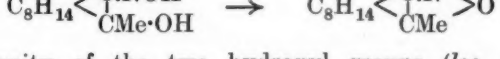
The principal reason for failing to improve on this process probably lies in the facility with which the unstable modification (m. p. 114°) changes into the less fusible isomeride (m. p. 152°). Transformation begins at the melting point and occurs also in cold aqueous alkali hydroxide, especially when the solution is exposed to light. It was later found that in ethereal solution diazomethane (J., 1908, **93**, 247), ferric chloride (J., 1913, **103**, 666) and probably magnesium methyl iodide (J., 1905, **87**, 236) effect the same change.

The configuration of these two monoximes of camphorquinone, as diagnosed by methods applied to (*a*) the stable form and (*b*) the Claisen mixture of stable and unstable forms, appears to be as follows :

syn-Modification (m. p. 152°). *anti*-Modification (m. p. 114°).

The determining factor in this diagnosis is the readiness with which anhydride formation takes place in a compound obtained from the less fusible modification and magnesium methyl iodide, suggest-



ing propinquity of the two hydroxyl groups (*loc. cit.*). The desirability of completing the inquiry by reviewing the behaviour of (*c*) the unstable form of *iso*nitrosocamphor led to the present investigation, which has incidentally revealed a simple method of producing that substance.

Several years ago an attempt was made by one of us to separate the components of the Claisen mixture by steam distillation. Following an observation that the low-melting, unstable hydrazone of camphorquinone (J., 1910, **97**, 2166) and the low-melting, unstable phenylhydrazone (J., 1911, **99**, 484) are volatile in steam and may thus be separated from their isomerides, the same relationship between the monoximes (*iso*nitrosocamphors) might have been expected. Unfortunately, however, although a small proportion of the low-melting oxime is removed from the freshly-prepared Claisen mixture by steam, the passage of its vapour is outpaced by the transformation of its hot aqueous solution into that of the stable isomeride. For the purpose of separating the low-melting oxime, therefore, this method is valueless, and an attempt to remove the more volatile substance by sublimation in a liquid air–charcoal vacuum was unsuccessful.

We have now found that the simplest of all possible methods, namely, fractional precipitation by acetic acid from the original solution of sodium derivatives, effects an excellent separation and incidentally confirms the conclusion (J., 1903, **83**, 526) that the Claisen mixture comprises equal parts of the two isomerides. This precipitation demands exactness, but had Claisen and Manasse used acetic acid instead of carbon dioxide for their attempted fractional precipitation, they might themselves have effected the separation, as they evidently suspected the existence of a low-melting, unstable compound in their product (*Annalen*, 1893, **274**, 71).

It has thus become possible to examine the action of magnesium

methyl iodide on the unstable *iso*nitrosocamphor as an individual, and the result shows that the α-oxime alone is formed. From the earlier paper (J., 1905, **87**, 232) it appeared that only the γ-oxime arose from stable *iso*nitrosocamphor, whilst the Claisen mixture gave the α- and γ-oximes associated with a third substance called the β-oxime. The α-oxime does not yield the anhydride when a solution in aqueous potassium hydroxide is boiled, and is thus distinguished from the β- and γ-oximes; and it is this distinction which appears to establish the above-mentioned configuration for the two forms of *iso*nitrosocamphor.

Hence the connexion between the α- and γ-oximes appears to be that of the *iso*nitroso-derivatives from which they spring, but the relationships of the β-oxime are less exact, as this is not produced from either form of *iso*nitrosocamphor alone, but only when they are associated in the Claisen mixture. The properties of this mixture in organic media suggest a loose union between the *syn*- and *anti*-modifications which is not disturbed by solvents, but is resolved by dissolution in alkali hydroxide; and we now believe that the so-called β-oxime is not an individual, but a mixture of the α- and γ-oximes inheriting the characteristic property of the Claisen mixture. This appears a more probable explanation of the experiments than the alternative, which would rest on an inverted configuration of the methyl and hydroxy-groups attached by the Grignard agent.

It also seems justifiable to conclude that formation of the α-oxime alone from low-melting *iso*nitrosocamphor, formerly conjectured but now definitely proved, confirms the *anti*-configuration for the latter substance, and supports the deductions regarding the eight oximino-derivatives from camphorquinone already made (Forster, J., 1913, **103**, 662). In view of recent work by Meisenheimer and his collaborators tending to subvert hitherto accepted generalisations on the geometrical isomerism of oximes, it is proper to point out that the above-mentioned conclusions depend on ring formation even more than upon preferential *cis*-interaction, and that the evidence from both sources is in harmony.

Experimental.

The Claisen Mixture.—Sodium wire (8·5 g.) was immersed in absolute ether (250 c.c.) in a flask (1·5 l.) fitted with a condenser and a drying-tube and surrounded by melting ice. Camphor (54 g.) was added in small quantities and when completely dissolved was followed in dim light by redistilled amyl nitrite (45 g.), also in small amounts. After the first few additions, the liquid became yellow and a tendency to froth was checked by agitation, and control

of temperature; subsequently added quota could be safely increased, and when all had been entered the reddish-brown product was left in ice during 1—2 hours, a small quantity of solid appearing. In semi-darkness, ice and water were added until a reddish-brown aqueous layer had separated from the pale yellow ethereal stratum, it being recalled that the sodium derivative of the unstable isomeride, when dissolved in water and exposed to light, is transformed into the stable modification. After removal of the aqueous layer, the ethereal portion was twice washed with water, which, when added to the alkaline fluid, increased its volume to 150 c.c. This in turn was extracted twice with small quantities of ether to remove borneol and unchanged camphor, being finally freed from ether by a current of air.

Separation of the Isomerides.—Dilute acetic acid (20%) was added in small quantities to the constantly shaken alkaline fluid at 0° until 72 c.c. had been used; the faintly yellow, crystalline precipitate was then filtered off, washed with ice-water and very dilute acetic acid, and again with ice-water. Dried in air, this product weighed 7·5 g. (m. p. 110—112°) and was the unstable *iso*nitrosocamphor. The filtrate with washings, now paler but still alkaline, acidified with acetic acid, yielded a colourless, crystalline precipitate (11·6 g.), m. p. 125—130°, the filtrate from which gave up 1·3 g. of stable *iso*nitrosocamphor (m. p. 149—152°) to ether. The fraction weighing 11·6 g. (m. p. 125—130°) was redissolved in 5% aqueous sodium hydroxide, and careful precipitation with 20% acetic acid gave 1·5 g. of the unstable derivative; a smaller quantity of this was obtained by completing the precipitation, passing steam through the product, and extracting the distillate with ether. Thus the separation gave 9—10 g. of unstable *iso*nitrosocamphor and 10—11 g. of the stable isomeride, while 22 g. of borneol and unchanged camphor were recovered from the original ethereal solution. It has been previously stated by one of us that the isomerides cannot be separated by fractional crystallisation from organic solvents; this was the experience of Claisen and Manasse, and our own confirms it. The intermediate fraction (m. p. 125—130°) from another experiment was extracted with hot petroleum (b. p. 60—80°), in which the low-melting form is freely soluble; but the undissolved portion remained a mixture (m. p. 125—128°) and the filtrate deposited a mixture (m. p. 122—125°).

Action of Magnesium Methyl Iodide.—The action of Grignard's agent on (*a*) the stable form and (*b*) the Claisen mixture having been previously observed, it remained to direct this on (*c*) the unstable form, for which purpose the fraction (m. p. 110—112°) obtained above was recrystallised from petroleum. Magnesium

(2 g. of clean turnings) immersed in dry, ice-cold ether (100 c.c.) was dissolved by portion-wise addition of methyl iodide (25 g.), unstable *iso*nitrosocamphor being then added in very small quantities to the constantly shaken liquid. Vigorous action accompanied by hissing and effervescence took place, the added solid becoming red and then dissolving whilst the ether became green. When about one-half the oxime had been added, the green colour suddenly changed to pale yellow and a viscous, dark-grey, heavy syrup appeared, increasing with further additions. Action became noticeably feebler, and the red solid produced on entering the concluding portions remained suspended above the syrup, but dissolved in the course of 24 hours. Ice and aqueous acetic acid were then added until the liquid was clear, and the ethereal portion was shaken with sodium carbonate (10%) and extracted four times (10 c.c. each) with sodium hydroxide (5%) to remove unchanged *iso*nitrosocamphor. The ethereal solution was then shaken twice (25 c.c. each time) with aqueous potassium hydroxide (25%), washed with water, dried, and allowed to evaporate in darkness. The crystalline residue, which had a slight camphoraceous odour, was powdered, mixed with a small quantity of low-boiling petroleum, and drained on earthenware. Recrystallisation of the product (3·2 g.) from aqueous alcohol gave colourless, glistening plates (m. p. 181°, instead of 178°) having $[\alpha]_D$ 86·6° (instead of 84·2°) in chloroform, falling to 69·7° (constant) during 24 hours in strong light. A solution in aqueous potassium hydroxide (10%) remained clear on boiling, and a solution in dilute sulphuric acid (10%) became turbid on boiling, from separation of the anhydride.

The compound is thus identified as the α-oxime (J., 1905, **87**, 237), and is the sole product of acting upon the unstable *iso*nitrosocamphor with magnesium methyl iodide, because the β- and γ-oximes were not present in the aqueous potassium hydroxide (25%) from which they were precipitated on the former occasion (*loc. cit.*). On allowing the chloroform solution of the α-oxime to evaporate after the diminished optical activity had become constant, the γ-oxime was obtained; it crystallised from petroleum in characteristic, sparingly soluble needles and also from boiling water. Solutions of the γ-oxime in aqueous potassium hydroxide (10%) and in dilute sulphuric acid (10%) became turbid when boiled, owing to anhydride formation.

An intimate mixture of the α- and γ-oximes melted mid-way between the melting points of the components, and a solution of this mixture in hot petroleum (b. p. 60—80°) deposited the snow-white, opaque nodules (m. p. 183·5—184·5°, instead of 183°) previously mistaken for an individual substance and called the β-oxime.

This material is very delusive. Its appearance is quite distinct from that of the α- and γ-oximes, and it changes completely into the γ-oxime when heated on the water-bath, although the α-oxime alone remains unchanged by this treatment. Moreover, the rotation of the α-oxime in chloroform falls to a point mid-way between the original angle and that given by the γ-oxime, remaining constant approximately at the value formerly ascribed to the β-oxime. Nevertheless, we believe the last-named substance to be a mixture.

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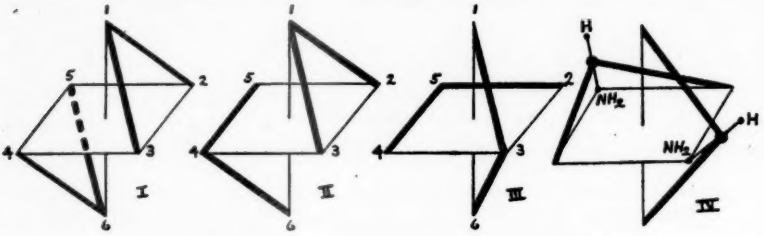
BANGALORE, S. INDIA. [*Received, September 13th*, 1926.]

CCCLII.—*The Configuration of the Bistriaminopropane Metallic Complexes.*

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

WE have previously described (*Proc. Roy. Soc.*, 1925, **107**, *A*, 80) a method by which αβγ-triaminopropane, $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$, can be prepared expeditiously and in high yield, and we have shown furthermore that this triamine co-ordinates with cobalt and rhodium to give complex compounds of the type of bistriaminopropanecobaltic chloride, $[Co\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2]Cl_3$, a compound in which two molecules of the aliphatic triamine have replaced the six molecules of ammonia in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$. On the basis of Werner's octahedral configuration of the hexamminocobaltic complex, it will be seen that the bistriaminopropanecobaltic complex should exist in three distinct isomeric forms. In the first two forms (I and II, where the position of the triamine molecules is indicated by the thick lines), each molecule of the triamine is bent at an angle of 60° about the central carbon atom, so that the three amino-groups become attached to the three corners of a triangular octahedron face: in the third form (III), the triamine molecule is bent at an angle of 90° about the central carbon atom, the three amino-groups being thus attached to the three corners of the square cross-section of the octahedron. The first isomeride has the two molecules of the triamine occupying the 2, 1, 3 : 4, 6, 5 positions (I), and the complex possesses therefore a plane of symmetry, and is not resolvable into optically active forms. The second isomeride has the triamine molecules in the 2, 1, 3 : 5, 4, 6 positions (II) and is therefore dissymmetric and should be capable of resolution into optically active forms. In the third isomeride—of completely different type from the former two—the triamine molecules occupy the 1, 3, 6 : 4, 5, 2

positions (III). This form would appear to have a plane of symmetry through the square cross-section 1, 3, 6, 5, of the octahedron.



Further consideration shows, however, that actually the triaminopropane molecules would not be placed symmetrically to the two cube planes of symmetry of the regular octahedron, because the central co-ordinating amino-group should give a lateral displacement to the central carbon atom, thus preventing the triamine molecule from coinciding with the cube plane of symmetry. This is shown in (IV), where the actual positions occupied by the central carbon atom and by the hydrogen atom and the amino-group attached to it are depicted. This lateral displacement of the central carbon atom by the β-amino-group would destroy the symmetry of the third isomeride, which should therefore also be resolvable into optically active forms. In the first isomeric form (I), this lateral displacement of the central carbon atom (at the 1 and 6 positions, respectively) occurs in the plane of symmetry, which is thus not affected.

Triaminopropane has now been co-ordinated with tervalent cobalt, tervalent rhodium, and bivalent nickel. The simple salts of the complexes so formed are in all cases highly crystalline, stable compounds, in which no trace of the above isomerism could be detected by macroscopic examination. It is therefore highly probable that one of the three isomerides is very much more stable than the other two, and is always formed to the almost complete exclusion of these. A somewhat similar case has recently been described by Morgan and Main Smith (J., 1925, **127**, 2030), who have co-ordinated ethylenediaminobisacetylacetone with cobalt to give diamminoethylenediaminobisacetylacetonecobaltic monochloride. Here the substituted ethylenediamine occupies four of the six co-ordination positions, and the complex so formed should exist in one symmetric and in two dissymmetric isomeric forms. The latter two were in this case actually isolated, but each passed rapidly into the symmetric and therefore more stable form: moreover, the presence of the latter stable form in the laboratory at once prevented further preparation and isolation of the dissymmetric and optically active isomerides.

Spatial considerations would indicate that triaminopropane, when co-ordinated to the three corners of a triangular face of the octahedron, should give a more stable arrangement than when co-ordinated to the three corners of a square cross-section. Isomerides I and II are therefore probably far more stable than III, and of these two the first, as the symmetric form, is in turn more stable than the second. We therefore consider it highly probable that all the complex salts of this triamine which we have prepared consist almost exclusively of the isomeride having the configuration I, the two molecules of the triamine occupying the 2, 1, 3 and the 4, 6, 5 positions, respectively.

The only evidence of the existence of isomeric forms that we have been able to obtain is that bistriaminopropanecobaltic *d*-camphor-β-sulphonate, after repeated crystallisation, does furnish a very faintly active chloride. The more soluble fractions, however, when reconverted into the iodide, give a *l*-camphorsulphonate which, after fractional crystallisation, furnishes a completely inactive chloride. This would suggest that the symmetric cobalt complex of configuration I may contain a very small proportion of a dissymmetric isomeride, probably of configuration II, but that this second isomeride is very easily either converted into the symmetric form or eliminated by fractional crystallisation.

Fractional crystallisation of the *d*-α-bromocamphor-π-sulphonate gave a completely inactive chloride. Werner found that the camphor- and bromocamphor-sulphonates of the metallic complexes frequently separated in mixed crystals, and to resolve, for example, the tris-αα′-dipyridylferrous complex and the trisethylenediaminerhodium complex, he had recourse to fractional crystallisation of their chlorotartrates (*Ber.*, 1912, **45**, 433, 1228), and in the case of the trisethylenediaminechromium complex, to fractional crystallisation of the camphor-α-nitronate (*ibid.*, p. 865). No crystalline chlorotartrate of the bistriaminopropanecobaltic complex could, however, be prepared, whilst fractional crystallisation of the camphor-α-nitronate gave no resolution.

The stability of the bistriaminopropane metallic complex is further shown by the fact that it is formed even when the metal is treated with only one molecule of the base, half the available metal thus not entering into combination with the amine under these conditions. Thus monochloropentamminocobaltic chloride, when treated with one molecule of the base, gives bistriaminopropanecobaltic chloride, and not triamminomonotriaminopropanecobaltic chloride, whilst nickel succinimide under similar conditions also gives solely the bistriaminopropanenickel salt.

EXPERIMENTAL.

In the formulæ of the following co-ordination compounds, the symbol " ptn " is used to denote one molecule of triaminopropane.

Improved Preparation of Bistriaminopropanecobaltic Chloride, $[Co\ ptn_2]Cl_3$.—A solution of triaminopropane trihydrochloride (20 g.) in 15% aqueous sodium hydroxide (71·4 c.c.) is added to a mixture of water (50 c.c.) and monochloropentamminocobaltic chloride (10 g.) or the equivalent quantity of monoaquopentamminocobaltic chloride. The whole is warmed on a water-bath for 3 hours, ammonia being freely evolved, and is then concentrated to small bulk, made just acid with hydrochloric acid, and filtered. The filtrate can be used for the preparation of most salts of the complex. Further evaporation gives the crystalline bistriaminopropanecobaltic chloride, whilst treatment with potassium thiocyanate solution gives the *thiocyanate*, $[Co\ ptn_2](SCN)_3$, which on recrystallisation from water is obtained in pale brown prisms, m. p. 286—288° (decomp.) (Found: C, 26·3; H, 5·4. $C_9H_{22}N_9S_3Co$ requires C, 26·3; H, 5·4%). The bistriaminopropanecobaltic complex is isolated in best yield by precipitation with potassium iodide as the far less soluble iodide, which we have already described (*loc. cit.*).

Bistriaminopropanecobaltic d-*camphor*-β-*sulphonate*,

$$[Co\ ptn_2](C_{10}H_{15}O{\cdot}SO_3)_3,$$

is of interest since it furnishes the only evidence so far obtained that the cobalt complex may contain a very small proportion of a dissymmetric isomeride. Aqueous solutions of the iodide of the complex and of the requisite amount of silver *d*-camphor-β-sulphonate were boiled together, the silver iodide was filtered off, and the solution evaporated to small bulk. The solution could not be induced to crystallise and finally gave a thick syrup. This was dried in a vacuum, and the product recrystallised four times from absolute alcohol. The *camphor*-β-*sulphonate* was thus obtained in orange-yellow crystals containing a molecule of alcohol of crystallisation {Found: $C_2H_5{\cdot}OH$, 4·85. $[Co\ ptn_2](C_{10}H_{15}SO_4)_3,C_2H_5{\cdot}OH$ requires $C_2H_5{\cdot}OH$, 4·7%. Found for the alcohol-free material: C, 46·2; H, 7·45. $C_{36}H_{67}O_{12}N_6S_3Co$ requires C, 46·4; H, 7·3%}. The alcohol-free material, which is markedly hygroscopic, shrinks at about 265° and finally melts at 285—286° (decomp.). A 2·960% aqueous solution had $\alpha + 1{\cdot}03°$ ($l = 2$), whence $[\alpha] = + 17{\cdot}4°$ and $[M] = + 162°$.*

Some of this material was dissolved in a minimum of water and a considerable excess of concentrated pure calcium chloride solution added. To the clear mixture was added a large quantity of alcohol;

* All rotations given in this paper are for the mercury yellow line ($\lambda = 5780$).

the precipitated bistriaminopropanecobaltic chloride, after being washed with warm alcohol and dried, was pure (Found: C, 20·8; H, 6·5. Calc. for $C_6H_{22}N_6Cl_3Co$: C, 20·9; H, 6·45%). For rotation measurements, only a short length of the very dilute orange-coloured solution could be used, otherwise the high absorption of light rendered accurate measurement impossible. A 3·088% solution of the chloride gave $\alpha + 0·22°$ ($l = 2$), whence $[\alpha] = + 3·6°$. The *d*-camphorsulphonate, when recrystallised from alcohol nine times, possessed the same melting point as above, and in 3·072% aqueous solution gave $\alpha + 1·10°$ ($l = 2$), whence $[\alpha] = + 17·9°$ and $[M] = + 166°$. The chloride obtained from this product was also faintly active, since a 5·452% aqueous solution gave $\alpha + 0·29°$ ($l = 2$), whence $[\alpha] = + 2·7°$. The *d*-camphorsulphonate remaining in the alcoholic mother-liquor from the nine recrystallisations was now recovered and converted into the iodide, and the latter was once recrystallised from water and then converted as before into the *l*-camphor-β-sulphonate. The latter was recrystallised four times from alcohol; the alcohol-free material began to shrink at about 265° and melted at 287—288° (decomp.). A 2·965% aqueous solution gave $\alpha - 1·03°$ ($l = 2$), whence $[\alpha] = - 17·4°$ and $[M] = - 162°$. This material gave, however, a completely inactive chloride.

These results were repeated, and once again the *d*-camphorsulphonate prepared from fresh iodide gave a faintly dextrorotatory chloride, but the *l*-camphorsulphonate, obtained by working up the mother-liquors *via* the iodide, gave an inactive chloride.

These results would indicate that the bistriaminopropanecobaltic complex does actually contain a very small proportion of a dissymmetric isomeride, probably having the configuration (II), and it is to the presence of this isomeride that the faint dextrorotation of the above chloride is due. This dissymmetric compound would be less stable and more soluble than its symmetric isomeride, and it is either converted into the latter or is left in solution when the *d*-camphorsulphonate residues are converted into the iodide, the latter recrystallised, and converted into the *l*-camphorsulphonate.

Bistriaminopropanecobaltic d-α-*Bromocamphor*-π-*sulphonate*, $[Co\ ptn_2](C_{10}H_{14}SO_4Br)_3$.—This was obtained in the usual way by the interaction of the iodide of the complex and the silver salt of the sulphonic acid. The concentrated aqueous solution of the sulphonate must be allowed to cool very slowly to obtain a crystalline deposit. The latter was recrystallised four times from water and was then obtained as a *pentahydrate* (Found: C, 34·3; H, 6·0. $C_{36}H_{64}O_{12}N_6Br_3S_3Co,5H_2O$ requires C, 34·4; H, 5·9%). The pentahydrate, when confined over calcium chloride at atmospheric

pressure for several days, gives a *dihydrate*, which is stable under these conditions (Found : C, 35·7; H, 5·6; H_2O, 3·1.

$$C_{36}H_{64}O_{12}N_6Br_3S_3Co,2H_2O$$

requires C, 35·9; H, 5·7; $2H_2O$, 3·0%). A 3·305% aqueous solution of the anhydrous sulphonate gave $\alpha + 4{\cdot}98°$ ($l = 2$), whence $[\alpha] = + 75{\cdot}3°$ and $[M] = + 880°$. The anhydrous sulphonate melts at 266—267° (decomp.). When the final crop of the sulphonate was mixed in strong aqueous solution with calcium chloride and the whole diluted with alcohol, the precipitated chloride of the complex was quite inactive.

Bistriaminopropanecobaltic d-*Camphor-α-nitronate*,

$$[Co\ ptn_2](C_{10}H_{14}O{\cdot}NO_2)_3.$$

—A solution of the chloride of the complex (7·0 g.) in water (80 c.c.) was mixed with a solution of ammonium nitrocamphor (14 g.) in water (100 c.c.). The pale yellow product which rapidly separated was recrystallised five times from water, and, when dry, was obtained in yellow, crystalline scales, m. p. 242—245° (decomp.) (Found : C, 52·2; H, 7·7. $C_{36}H_{64}O_9N_9Co$ requires C, 52·3; H, 7·8%). An aqueous solution of the fifth crop of the camphornitronate gave an inactive bromide of the complex.

Attempts were made to prepare the chlorotartrate of the cobalt complex by shaking an aqueous solution of the chloride with silver tartrate (1 mol.). The filtered solution was evaporated to small bulk and finally in a vacuum over sulphuric acid. A small crop of the chloride itself then separated, but no further crystalline product could be isolated.

Bistriaminopropanenickelous Iodide, $[Ni\ ptn_2]I_2$.—Triaminopropane trihydrochloride (11·4 g.) dissolved in warm 33% aqueous sodium hydroxide (16·4 c.c.) was added to a hot solution of nickel succinimide (6·0 g.) in alcohol (180 c.c.). The solution, which rapidly became reddish-blue, was evaporated to small bulk with the occasional addition of water until no alcohol remained. It was then added to saturated aqueous potassium iodide solution : the red precipitate, on recrystallisation from hot water, gave *bistriaminopropanenickelous iodide* as pale red, crystalline scales, which, when heated, darken at about 290° but do not melt below 300° (Found : C, 14·8; H, 4·6; I, 51·8; Ni, 11·9. $C_6H_{22}N_6I_2Ni$ requires C, 14·7; H, 4·5; I, 51·7; Ni, 12·0%).

Bistriaminopropanenickelous Sulphate Pentahydrate,

$$[Ni\ ptn_2]SO_4,5H_2O.$$

—Hot aqueous solutions of the iodide (9·0 g.) and silver sulphate (5·7 g.) were mixed, filtered, and evaporated to very small bulk. On cooling, the hydrated *sulphate* separated as deep red crystals (Found : C, 16·9; H, 7·6; SO_4, 23·0; H_2O, 21·2. $C_6H_{22}O_4N_6SNi,5H_2O$

requires C, 17·0; H, 7·6; SO_4, 22·7; $5H_2O$, 21·3%). The sulphate loses its water of crystallisation readily at 90° in a vacuum, and the anhydrous sulphate does not melt below 300°. The filtrate from the recrystallisation of the sulphate was diluted with alcohol until a faint turbidity appeared; a further crop of the pentahydrate then separated slowly in large, deep red crystals (Found : SO_4, 22·7%).

Many attempts were made to prepare triamminotriaminopropanecobaltic chloride, $[Co(NH_3)_3ptn]Cl_3$, by treating roseo- and purpureocobalt chloride with one molecular proportion of the base : these experiments always gave, however, the bistriaminopropanecobaltic salts, the remainder of the metal separating as the hydroxide. Similar experiments were made with nickel succinimide with the object of preparing salts in which the metal would show a co-ordination number of 4, such as aquotriaminopropanenickel chloride, $[NiH_2O\ ptn]Cl_2$, or of 6, such as triamminotriaminopropanenickel chloride, $[Ni(NH_3)_3\ ptn]Cl_2$: these experiments also always gave the bistriaminopropanenickel salts and a residue of a simple basic nickel salt.

Triaminopropane Dihydrochloride Monohydriodide, $C_3H_5(NH_2)_3,2HCl,HI$. —This mixed salt of the triamine is here placed on record. When a highly concentrated aqueous solution of triaminopropane trihydrochloride is treated with saturated potassium iodide solution, the *dihydrochloride monohydriodide* slowly separates. It crystallises from water in fine, white crystals, m. p. 303—304° (decomp.), which are very soluble in water (Found : C, 12·7; H, 4·9; N, 14·3; 2Cl + I, 68·4. $C_3H_{14}N_3Cl_2I$ requires C, 12·4; H, 4·9; N, 14·5; 2Cl + I, 68·2%). ββ′β″-Triaminotriethylamine trihydrochloride under similar conditions gives the monohydrochloride dihydriodide of the base (Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 449).

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CCCLIII.—*The Complex Salts of αβγ-Triaminopropane with Copper and Platinum.*

By FREDERICK GEORGE MANN.

MOST complex salts of bivalent copper can be grouped into two classes, *viz.*, those in which the metal shows a co-ordination number of 4, such as tetramminocupric chloride, $[Cu(NH_3)_4]Cl_2$, and bisethylenediaminecupric chloride, $[Cu(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2]Cl_2$; and those in which it shows a co-ordination number of 6, such as hex-

amminocupric chloride, $[Cu(NH_3)_6]Cl_2$, and trisethylenediaminecupric chloride, $[Cu(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3]Cl_2$. Salts of the latter class are, however, considerably less stable than those of the former class, and usually revert readily, for instance, on attempted recrystallisation from water, to the corresponding compounds in which the copper has a co-ordination number of 4. It has been shown in the previous paper (p. 2676) that the bistriaminopropane metallic complex salts possess great stability, and that bistriaminopropanenickel iodide, $[Ni\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2]I_2$, for instance, shows no perceptible tendency to revert to a compound in which the nickel shows a co-ordination number of 4 : in fact, no such compounds have yet been isolated. It was therefore considered probable that a compound of the type of bistriaminopropanecupric chloride, $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2]Cl_2$, would also be sufficiently stable to allow of its isolation and purification, and attempts were made to prepare such a compound in the hope that it might show the isomerism which the corresponding cobalt, rhodium, and nickel salts had failed to reveal.

When triaminopropane was added to an aqueous solution of a cupric salt, co-ordination at once occurred with the production of the usual characteristically deep violet colour. From such a solution, however, no complex salt of triaminopropane and copper, in which the latter shows a co-ordination number of 6, could be obtained. Instead, two complex salts of unexpected and novel types, in both of which the metal shows a co-ordination number of 4, were isolated. If copper, whilst showing a co-ordination number of 4, is to be completely saturated with a triamine, three atoms of the metal should unite with four molecules of the base : a complex of this type has now been isolated, for when potassium iodide was added to the above violet solution, *tetratriaminopropanetricupric hexaiodide* (I) slowly separated. This hexaiodide, and the corresponding *hexathiocyanate*, which has also been prepared, are quite

(I.) $[Cu_3\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_4]I_6$.

(II.) $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN\}_2](SCN)_2$.

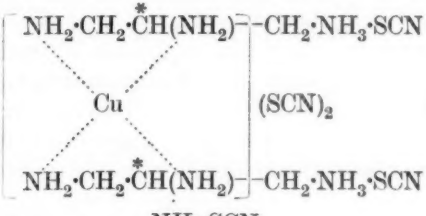
(III.) $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2,HSCN){\cdot}CH_2{\cdot}NH_2\}_2](SCN)_2$.

insoluble in cold water, as would be expected in view of their high molecular weight, and slowly decompose when boiled with water.

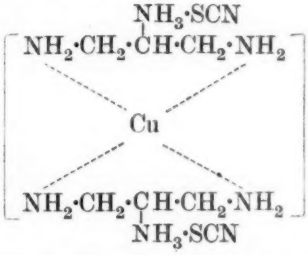
If, however, an aqueous solution of potassium thiocyanate acidified with acetic acid is added to the original violet copper solution, there separates a highly crystalline, stable compound, which can be obtained pure by recrystallisation from hot water. This compound is *bis*(*triaminopropanemonothiocyanate*)*cupric thiocyanate* (II), in which the copper is linked to two molecules of the triamine but,

as it still has a co-ordination number of 4, to only two amino-groups in each molecule of the triamine, the third amino-group in each case forming a salt with thiocyanic acid.† The complex itself is here bivalent, but since the thiocyanate radicals joined to the unco-ordinated amino-groups are also ionised, the compound in solution gives four thiocyanate ions. Two possibilities arise here. The copper may be co-ordinated to the αβ-diamino-groups, leaving the γ-amino-group free to form the thiocyanate salt, as in (II), or the copper may co-ordinate with the αγ-diamino-groups, leaving the β-amino-group free to form the thiocyanate, as in (III).

In the former compound (II), the triamine is acting, for co-ordination purposes, as a substituted ethylenediamine, and gives with the copper a five-membered ring (IV), whilst in the latter compound (III), the triamine is acting as a substituted trimethylenediamine, and thus gives with the metal a six-membered ring (V). For this reason, it is to be expected that the compound (II) would prove rather more stable than (III). On the other hand, consideration of the constitutional formulæ of the two compounds shows that the latter, having the αγ-diamino co-ordination linking, possesses far greater symmetry than the former and might therefore be of at least equal stability. Thus if the copper is co-ordinated through the αβ-diamino-groups of the triamine molecule, the γ-amino-groups, which form the thiocyanate salts, are not actually part of the metallic complex, and the compound (II) may be written in full as (IV). The two carbon atoms marked * are now



(IV.)



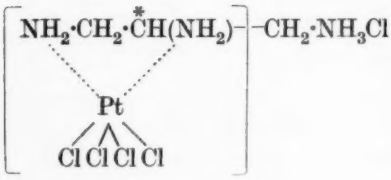
(V.)

† This compound may be compared with triglycerylcupric sulphate, $[Cu\{HO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH\}_3]SO_4$, where only two of the three hydroxy-groups in the trihydroxypropane molecule are co-ordinated to the metal.

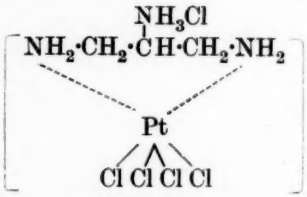
asymmetric, since they are linked on one side to an aminomethyl group ($-CH_2 \cdot NH_2 \cdots$) and on the other to a methylene-ammonium radical ($-CH_2 \cdot NH_3-$). The compound should therefore be capable of existing in dextro-, lævo-, racemic, and meso-forms. Moreover, if the four co-ordination valencies of the copper atom are directed to the apices of a regular tetrahedron, the copper atom is itself asymmetric, and the dextro-, lævo-, and meso-compounds should each exist in two forms, in which the copper has the *d*- and the *l*-configuration, respectively.

The compound having the $\alpha\gamma$-diamino co-ordination linking (V) has, on the other hand, a highly symmetric complex containing no asymmetric carbon or copper atoms, and might therefore, in spite of its six-membered ring, prove even more stable than that shown in (II). The constitution of the compound would be decided by its resolution into optically active forms, but in view of the intense violet colour of its solutions, no such attempts have yet been made.

This co-ordination of a metallic atom to two of the three amino-groups of triaminopropane is not limited to copper. It has been shown by Curtius and Hesse (*J. pr. Chem.*, 1900, **62**, 232) that triaminopropane trihydrochloride gives a chloroplatinate of composition $C_3H_5(NH_2)_3,3HCl,PtCl_4$. If the chloroplatinate is boiled in aqueous solution with an excess of the trihydrochloride of the base, a crystalline, canary-yellow compound, having the composition $C_3H_5(NH_2)_3,HCl,PtCl_4$, separates with a molecule of water of crystallisation, which may be easily driven off. This suggests that here again the metal has co-ordinated with two of the three amino-groups, leaving the third free to form a hydrochloride, and that the compound is actually *tetrachloro(triaminopropane monohydrochloride) platinum*, $[Cl_4PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2,HCl]$, having the constitution (VI) or (VII). Here the complex itself, consisting of quadrivalent platinum co-ordinated to two basic and



(VI.)



(VII.)

four acidic groups, is neutral and non-ionic, but the unco-ordinated amino-group, by uniting with hydrogen chloride to give a substituted ammonium chloride, furnishes one chloride ion. This is

confirmed by the fact that when the compound is treated with chloroplatinic acid, this unco-ordinated amine-hydrochloride group reacts normally to give a chloroplatinate of the composition

$$\{[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2)-]-CH_2{\cdot}NH_2\}_2,H_2PtCl_6.$$

Here again, if the platinum in the parent compound is co-ordinated to the αβ-diamino-groups, as shown in (VI), the carbon atom marked * becomes asymmetric, although the complex itself may possess a plane of symmetry.† If, on the other hand, the metal is linked to the αγ-diamino-groups, as in (VII), no asymmetric carbon atom exists. This platinum compound is thus simpler in type than the previous copper compound, and its resolution into optically active forms should decide whether in this type of complex salt the metal is co-ordinated to the αβ- or the αγ-diamino-groups. Such attempts are now being made.

Experimental.

Tetratriaminopropanetricupric Hexaiodide (I).—A solution of triaminopropane trihydrochloride monohydrate (19·0 g.) in 15% aqueous sodium hydroxide (64·0 c.c.) was added to one of hydrated cupric sulphate (10·0 g.) in water (50 c.c.); to the deep violet solution, after 2 hours, cold saturated potassium iodide solution was added. After 12 hours, the precipitate was filtered off, washed with water until the wash liquors were colourless, and dried. *Tetratriaminopropanetricupric hexaiodide* was thus obtained as a fine, slate-blue powder, m. p. 236—237° (decomp.) (Found: C, 11·0; H, 3·4; N, 12·7; I, 57·8; Cu, 14·4. $C_{12}H_{44}N_{12}I_6Cu_3$ requires C, 11·0; H, 3·4; N, 12·8; I, 58·2; Cu, 14·6%). Warming the original solution before the addition of the potassium iodide resulted in the hexaiodide giving slightly low values for iodine, due presumably to hydrolysis.

When a solution of potassium thiocyanate, freshly prepared in cold water, was added to the original solution, slow precipitation occurred and continued for several hours. The first crop consisted of *tetratriaminopropanetricupric hexathiocyanate*,

$$[Cu_3\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_4](SCN)_6,$$

mixed with the dithiocyanate described below: it was washed with water to remove the soluble dithiocyanate. The second crop contained much less dithiocyanate and required less washing to

† Lateral displacement of the central carbon atom in the propane molecule by the β-amino-group (discussed in the previous paper) might destroy this plane of symmetry and render the complex itself dissymmetric.

give the pure *hexathiocyanate*. The latter was thus obtained in small, deep violet crystals, m. p. 184—185° (decomp.) (Found: C, 24·3; H, 4·9; N, 27·8; S, 21·7; Cu, 21·1. $C_{18}H_{44}N_{18}S_6Cu_3$ requires C, 24·1; H, 4·95; N, 28·2; S, 21·5; Cu, 21·3%).

Bis(triaminopropanemonothiocyanate)cupric Thiocyanate (II).—A concentrated aqueous solution of potassium thiocyanate diluted with a small quantity of acetic acid was added to the original violet copper solution; deep violet crystals rapidly separated. After some time, these were filtered off, washed, and recrystallised from water, the *thiocyanate* being thus obtained in long needles or prisms, m. p. 174—175° (decomp.). For analysis, the ionised thiocyanate was estimated by precipitation with silver nitrate (*a*) in cold aqueous solution containing a few drops of dilute nitric acid, which destroyed the complex salt, (*b*) in cold neutral solution, in which the complex was stable [Found in different preparations: C, 25·2, 25·2; H, 5·1, 5·1; N, 29·4; S, 26·8; Cu, 13·4, 13·4; SCN (*a*) 48·8, (*b*) 49·3. $C_{10}H_{24}N_{10}S_4Cu$ requires C, 25·2; H, 5·1; N, 29·4; S, 26·9; Cu, 13·4; 4SCN, 48·8%].

If the potassium thiocyanate solution used in the preparation has previously been kept for several days or heated on the water-bath for a few hours, it becomes sufficiently acid by partial hydrolysis to precipitate the above thiocyanate, without any addition of acetic acid. The salt separates under these conditions more slowly than when the potassium thiocyanate contains acetic acid, and may form crystals 1—2 cm. in length.

Bis(triaminopropanemonohydrobromide)cupric Bromide Dihydrate, $[Cu\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HBr\}_2]Br_2,2H_2O$.—A warm, aqueous solution of the thiocyanate was treated with silver nitrate (4 mols.) and the filtered solution was evaporated to very small bulk, and, when cool, diluted with a saturated aqueous solution of sodium bromide. The crystalline bromide which separated was too soluble in water to be recrystallised. Its aqueous solution was therefore diluted with alcohol until faintly turbid and then filtered. On keeping over-night, it deposited the *bromide* in deep violet crystals (Found: C, 12·2; H, 4·7; N, 13·7; Br, 53·5; H_2O, 6·3. $C_6H_{28}O_2N_6Br_4Cu$ requires C, 12·0; H, 4·7; N, 14·0; Br, 53·3; $2H_2O$, 6·0%).

Tetrachloro(triaminopropanemonohydrochloride)platinum Monohydrate, $[Cl_4PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCl]H_2O$.—An aqueous solution containing triaminopropane trihydrochloride (2 mols.) and chloroplatinic acid was boiled under reflux for 3 hours, the orange-red colour becoming pale yellow, then heated on the water-bath for 3 hours with the occasional addition of water, and finally evaporated to small bulk; fine, yellow crystals separated on cooling.

These, when recrystallised from a little water, gave *tetrachloro-(triaminopropanemonohydrochloride)platinum monohydrate* as fine, canary-yellow crystals, which lost water of crystallisation in a vacuum at 110° (Found in different preparations: C, 7·6, 7·5; H, 2·9, 2·9; Pt, 40·6, 40·6; Cl, 37·0, 37·1; H_2O, 3·85. $C_3H_{14}ON_3Cl_5Pt$ requires C, 7·5; H, 2·9; Pt, 40·6; Cl, 36·9; H_2O, 3·75%). The hydrate darkened at about 255° and melted at 272—273° (decomp.), whilst the anhydrous material darkened in the same way and melted at 273—274° (decomp.): the dehydration had not therefore changed the essential nature of the compound. The molecule of water of crystallisation may be attached to the complex itself or to the free amine-hydrochloride group.

Tetrachloro(triaminopropanemonohydrochloride)platinum Chloroplatinate Monohydrate,

$$\{[Cl_4PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot]\cdot CH_2\cdot NH_2,HCl\}_2PtCl_4,H_2O.$$

—A cold concentrated aqueous solution of the above monohydrochloride was added to a strong solution of chloroplatinic acid which had previously been nearly neutralised with sodium carbonate. A fine precipitate slowly separated and when recrystallised from a little hot water gave the *chloroplatinate* as a fine yellow-orange coloured powder, which did not melt below 290°: the original solution slowly gave a further crop of the chloroplatinate as fine needles (Found: C, 5·5; H, 2·1; Cl, 38·9; Pt, 45·7. $C_6H_{26}ON_6Cl_{14}Pt_3$ requires C, 5·6; H, 2·05; Cl, 38·8; Pt, 45·7%).

Tetrabromo(triaminopropanemonohydrochloride)platinum Monohydrate, $[Br_4PtNH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCl]H_2O$.—An aqueous solution of the original tetrachloro-compound was mixed with a saturated aqueous solution of potassium bromide, and after 24 hours the yellowish-red crystals which had separated were collected and recrystallised from a little water, in which they were very soluble. *Tetrabromo(triaminopropanemonohydrochloride)platinum monohydrate* was thus obtained in fine, orange crystals, which darkened at about 245° and melted at 262—263° (decomp.) [Found: C, 5·4; H, 2·1; (4Br + Cl), 53·8; Pt, 29·8. $C_3H_{14}ON_3ClBr_4Pt$ requires C, 5·5; H, 2·1; (4Br + Cl), 53·9; Pt, 29·6%].

Tetrachloro(triaminopropanemonohydrochloride)platinum gave in aqueous solution an unexpected reaction with potassium thiocyanate, since the mixed solutions slowly deposited potassium platinithiocyanate, $K_2Pt(SCN)_6$ (Found, for the recrystallised material: C, 11·7; N, 13·2. Calc. for $C_6N_6S_6K_2Pt$: C, 11·6; N, 13·5%). Ammonium thiocyanate solution similarly gave ammonium platinithiocyanate, $(NH_4)_2Pt(SCN)_6$ (Found: Pt, 33·8. Calc. for $C_6H_8N_8S_6Pt$: Pt, 33·7%).

Potassium and ammonium chloride solutions did not give pre-

cipitates of the corresponding chloroplatinates even after several days: these solutions on keeping would not, however, develop the acid properties of the thiocyanate solutions.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 30th*, 1926.]

CCCLIV.—*Preparation of Hydroxybenzophenones and Hydroxyxanthones.*

By HAROLD ATKINSON and ISIDOR MORRIS HEILBRON.

NISHIKAWA and ROBINSON have shown (J., 1922, **121**, 839) that the Hoesch reaction, applied to the condensation of phloroglucinol with salicylonitrile, leads to 2 : 4 : 6 : 2′-tetrahydroxydiphenyl ketimine hydrochloride, which, on boiling with water, gives the free base. The ketimine is readily hydrolysed by aqueous sodium hydroxide, yielding 1 : 3-dihydroxyxanthone, no tetrahydroxybenzophenone being produced (compare Karrer, *Helv. Chim. Acta*, 1921, **4**, 992). Hydroxyxanthones, however, are not invariably formed by this method, since Shoesmith and Haldane (J., 1924, **125**, 113) isolated only 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone by the condensation of resorcinol with diacetyl-β-resorcylonitrile and subsequent hydrolysis of the ketimine hydrochloride with 25% sulphuric acid. These authors found that the compound described by Marcus (*Ber.*, 1891, **24**, 3652) as β-resorcylonitrile would not condense with resorcinol; hence their use of the diacetyl derivative. With a view to obtain several hydroxyxanthones for spectrographic examination, the applicability of the Hoesch reaction to (*a*) salicylonitrile and resorcinol, (*b*) salicylonitrile and pyrogallol, and (*c*) β-resorcylonitrile and pyrogallol has now been tested, and the work of Nishikawa and Robinson has been repeated. We are able to confirm the data of these investigators in all details, but, except in the case of 1 : 3-dihydroxyxanthone, we find that no reaction takes place unless the hydroxy-groups of the aromatic nitrile are protected. When the acetyl derivatives are employed, the reaction takes the usual course; the presence of the acetyl group, however, gives rise to various side reactions which complicate the isolation of the required products and also considerably reduce the yield. In the synthesis carried out by Shoesmith and Haldane (*loc. cit.*), resacetophenone and β-resorcylamide also were isolated, the production of the former compound being attributed to the formation of acetyl chloride during the reaction. Analogously, when pyrogallol is condensed with diacetyl-β-resorcylonitrile, gallacetophenone

is formed together with a red colouring matter seemingly identical with that obtained when acetyl chloride reacts with pyrogallol (compare Knoll & Co., *Centralbl.*, 1900, I, 270).

In none of the condensations were we able to isolate the intermediate product (ketimine hydrochloride or free ketimine) in a condition giving analytical values reconcilable with those demanded by the respective compounds. This failure may be attributed to the partial removal of acetyl groups during the condensation, for it has been found that, in addition to the direct evidence of the production of gallacetophenone, on boiling the condensation products with water, the hydroxy- and not the acetoxy-benzophenones are produced. Moreover, in the reaction between *o*-acetoxybenzonitrile and pyrogallol, 3 : 4-dihydroxyxanthone has been obtained directly. This can be attributed only to the formation of 3 : 4-dihydroxyxanthyl ketimine hydrochloride, $O<\begin{matrix}C_6H_4\\C_6H_2(OH)_2\end{matrix}>C{:}NH,HCl$, during the initial condensation, since treatment of 2 : 3 : 4 : 2′-tetrahydroxybenzophenone with water alone at 100° does not bring about ring closure.

Experimental.

3-*Hydroxyxanthone*.—Through a solution of *o*-acetoxybenzonitrile (7·5 g.) and dry resorcinol (10 g.; 2 mols.) * in pure dry ether (100 c.c.) containing freshly-fused zinc chloride (2 g.), dry hydrogen chloride was passed for 6 hours; a viscous syrup began to be deposited after about 4 hours. The mixture was kept at 0° for a week, more syrup being precipitated. The ether was then decanted, the residue twice triturated with dry ether, and all solvent removed under reduced pressure. Attempts to isolate a pure ketimine hydrochloride having failed, the gummy condensate was dissolved in hot water (100 c.c.) and treated with an excess of potassium acetate, which caused immediate precipitation of an amorphous, yellow solid, presumably the free ketimine. This compound crystallised from dilute alcohol in orange needles (m. p. 150—153°) the nitrogen content of which did not agree with that of 2 : 4-dihydroxy-2′-acetoxydiphenyl ketimine (Found: N, 3·5. $C_{13}H_{15}O_4N$ requires N, 5·2%). The precipitate was therefore boiled with an excess of *N*/2-sodium hydroxide, until the evolution of ammonia had ceased, and the cooled solution was acidified with dilute hydrochloric acid. The yellow, amorphous precipitate was dried, and repeatedly extracted with boiling xylene; 3-hydroxyxanthone, which separated from the xylene solution, crystallised from dilute alcohol in colourless needles (yield, 1·8 g.), m. p. 246°, giving a blue

* The use of 2 mols. of the phenol to 1 mol. of the nitrile increased the yield.

fluorescence in alkaline solution. Kostanecki and Nessler (*Ber.*, 1891, **24**, 3981) and Ullmann and Denkler (*Ber.*, 1906, **39**, 4332) give m. p. 242°.

The aqueous filtrate from which the xanthone had been separated slowly deposited pale yellow needles (0·5 g.), m. p. 133—134°, which had all the properties of 2 : 4 : 2′-trihydroxybenzophenone (compare Michael, *Ber.*, 1881, **14**, 658).

2 : 3 : 4 : 2′-*Tetrahydroxybenzophenone.*—This compound was prepared from pyrogallol (10 g.) and *o*-acetoxybenzonitrile (7·5 g.) by the method described above. The syrupy condensate, after removal of all the ether, was dissolved in cold water, and the solution strongly acidified with hydrochloric acid; bright yellow needles, m. p. 182—184°, then separated. These were boiled with water for 1 hour; the solution, on cooling, deposited glistening, bronze plates mixed with a red dye. From an ethereal solution of the mixture, light petroleum precipitated a deep red, semi-solid material, which was removed; the filtrate was evaporated to dryness and after a preliminary purification by means of alcohol and animal charcoal the residue was crystallised from hot water. 2 : 3 : 4 : 2′-Tetrahydroxybenzophenone was thus obtained in lustrous, yellow plates, m. p. 100°, which, after drying in the steam-oven, melted at 149° (compare Graebe and Eichengrun, *Ber.*, 1891, **24**, 969). Yield, 18·5%.

The oily dye previously mentioned, further quantities of which were obtained on boiling the acid filtrate from which the supposed ketimine salt had crystallised, was extracted with boiling xylene, and from the extract, on cooling, a yellow, crystalline solid was deposited. Treatment of this with boiling water removed a further quantity of tetrahydroxybenzophenone and left a very small, insoluble residue which, on crystallisation from dilute alcohol, deposited yellow needles, m. p. 238—240°, agreeing in properties with the 3 : 4-dihydroxyxanthone obtained by Graebe and Eichengrun (*loc. cit.*). In addition to these two substances, gallacetophenone, m. p. 168°, was isolated in minute quantity by repeated extraction of the boiled aqueous filtrate, after separation of the red oil, by means of ether. It yielded a semicarbazone, m. p. 224°, in agreement with that found by Fischer (*Ber.*, 1909, **42**, 1015).

2 : 3 : 4 : 2′ : 4′-*Pentahydroxybenzophenone.*—Pyrogallol (12 g.) and diacetyl-β-resorcylonitrile (10 g.) were dissolved in dry ether (150 c.c.) together with freshly-fused zinc chloride (2 g.), and the whole was treated with dry hydrogen chloride. The solution became turbid after 7 hours and a yellow, crystalline solid separated. After standing in the ice-chest for 4 days, the ether was decanted and the residual mixture of crystalline solid and syrup freed from ether and

boiled for 2 hours with water. On cooling, a red, crystalline mass separated and this, after drying, was extracted with boiling xylene. The pink, crystalline solid (2·7 g.) which separated on cooling was recrystallised from dilute alcohol; the pentahydroxybenzophenone then separated in yellow needles which softened at 180° and melted at 187°. The compound contains 2 mols. H_2O which are removed by heating at 110°. The alkaline solution of the compound is bright yellow and exhibits no fluorescence, but on keeping the colour changes to greenish-yellow and finally to dark olive-green (Found : C, 52·6, 52·3; H, 4·7, 4·7; H_2O, 11·6. Calc. for $C_{13}H_{10}O_6,2H_2O$: C, 52·4; H, 4·7; H_2O, 12·1%). The melting point given for this substance in the patent specifications (Badische Anilin- und Soda-Fabrik, D.R.-PP. 49149, 50451) is 168—170°. After removal of the pentahydroxybenzophenone, the aqueous solution, on extraction with ether, yielded a small quantity of gallacetophenone.

3 : 6-*Dihydroxyxanthone*.—The condensation of resorcinol and diacetyl-β-resorcylonitrile was carried out as detailed by Shoesmith and Haldane (*loc. cit.*), but *N*/2-sodium hydroxide was used to hydrolyse the ketimine hydrochloride. On acidification, a solid separated from which 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone was removed with boiling water, leaving a brown, amorphous residue; this crystallised from alcohol, after charcoal treatment, in faintly brown needles. The substance, which did not melt below 300° and was only formed in 1% yield, showed all the properties of 3 : 6-dihydroxyxanthone, the alkaline solution of which is characterised by an intense violet fluorescence (compare Meyer and Conzetti, *Ber.*, 1897, **30**, 969).

In conclusion, we desire to thank the Council of the Department of Scientific and Industrial Research for a grant to one of us (H. A.) in aid of this research.

THE UNIVERSITY, LIVERPOOL. [*Received, July 16th*, 1926.]

CCCLV.—*Nitration of Fluorene. 2 : 5-Dinitrofluorene.*

By GILBERT T. MORGAN and REUBEN WILLIAM THOMASON.

IN 1876, the hydrocarbon fluorene was nitrated in glacial acetic acid with fuming nitric acid to yield a dinitrofluorene which has been examined since by several investigators who record melting points for this product ranging from 199° to 260° (*Ann. Chim. Phys.*, 1876, **7**, 498; Fittig and Schmitz, *Annalen*, 1878, **193**, 140; Barth and Goldschmidt, *Ber.*, 1878, **11**, 849; Meyer, *ibid.*, 1912, **45**, 1632).

This variation in fusibility suggests that the product is a mixture and we have accordingly attempted to separate its components. On crystallisation from glacial acetic acid, the crude material was apparently homogeneous and decomposed vigorously at 198°, but fractional crystallisation from this solvent led to a separation of two dinitrofluorenes of which the less soluble decomposed energetically at 269° and yielded on oxidation 2 : 7-dinitrofluorenone, a substance of known constitution obtained by Schmidt and Bauer from the corresponding dinitrophenanthraquinone (*Ber.*, 1905, **38**, 3746). This identity characterised the less fusible dinitro-compound as 2 : 7-*dinitrofluorene*.

The more soluble isomeride, which was present in the crude nitration product to a smaller extent, melted at 207° and on oxidation furnished a dinitrofluorenone of unknown constitution melting at 241°. Since the 2 : 4-, 2 : 7-, and 4 : 5-dinitrofluorenones have been obtained, these orientations of nitro-groups in the new dinitrofluorene are excluded. Moreover, the new product is not identical with the 1 : 8- or 2 : 9-dinitrofluorene already recorded.

When fluorene is nitrated under mild conditions, 2-nitrofluorene is obtained, that is, the phenylene group directs the nitro-group into the other aromatic nucleus in the para-position with respect to the mutual linking of the two benzene rings.

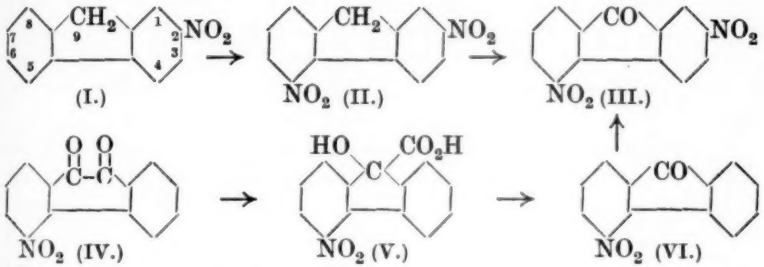
In the dinitration of fluorene, the production of 2-nitrofluorene may be regarded as the first stage. The second nitro-group enters the other ring and, as the phenylene radical rather than the methylene group is the directing influence, the entrant group will go into the ortho- and para-positions. Experiments show that the entry is mainly (85%) into the para-position, giving rise to 2 : 7-dinitrofluorene, but the by-product, the new dinitrofluorene, may result from an entry of the second nitro-group into the 5- or ortho-position, in which case the new isomeride would be 2 : 5-*dinitrofluorene*.

Carefully purified 2-nitrofluorene was nitrated further in glacial acetic acid, the main product being 2 : 7-dinitrofluorene; there was a smaller proportion of the new dinitrofluorene and some unchanged 2-nitrofluorene. This experiment indicates that one nitro-group in the new dinitrofluorene is in position 2.

To determine the orientation of the second nitro-group, the following synthesis has been carried through : Phenanthraquinone was nitrated and 4-nitrophenanthraquinone (IV) was carefully separated from the isomeric 2-nitrophenanthraquinone and converted into 4-nitrodiphenyleneglycollic acid (V) by the benzil–benzilic acid reaction. The carboxy-acid was decomposed by boiling with water into 4-nitrofluorenone (VI, positions 4 and 5 being identical in the molecule). When 4-nitrofluorenone (VI)

was nitrated, it yielded the new dinitrofluorenone (m. p. 241°), which is thus shown to be 2 : 5-*dinitrofluorenone* (III). And since this ketone is also obtained by oxidising the new dinitrofluorene, this derivative must be 2 : 5-*dinitrofluorene* (II).

The demonstration of this constitution is summarised in the following diagram :



EXPERIMENTAL.

Ten g. of fluorene were added gradually to 50 c.c. of fuming nitric acid, diluted with 50 c.c. of glacial acetic acid and maintained at the laboratory temperature. The solid product was filtered through glass wool, washed with cold water, and boiled with glacial acetic acid to dissolve the more soluble portion. The solution, filtered from undissolved dinitro-compound, was allowed to crystallise and this fractionation repeated until the more soluble 2 : 5-*dinitrofluorene* (II) was obtained in long, straw-coloured needles, m. p. 207°. A further quantity of this isomeride was obtained by pouring into water the original nitration liquors, the precipitated solid being crystallised repeatedly from glacial acetic acid (Found : C, 60·8; H, 3·1; N, 11·0. $C_{13}H_8O_4N_2$ requires C, 60·9; H, 3·1; N, 10·9%).

The less soluble portion of the above preparation was also crystallised repeatedly from glacial acetic acid; yellow needles of 2 : 7-*dinitrofluorene* were then obtained which became slightly discoloured at 238° and decomposed vigorously at 269°.

For the purpose of identifying one of its nitro-groups, 2 : 5-dinitrofluorene was also obtained from 2-nitrofluorene (*Ber.*, 1884, **17**, 107),. the latter nitro-compound being prepared by adding four times the calculated quantity of nitric acid (*d* 1·4) to a cold saturated solution of fluorene in glacial acetic acid. The hydrocarbon separated gradually, but was redissolved by warming on the water-bath. After 12 hours, the nitration mixture gave a practically quantitative yield of 2-nitrofluorene, which was purified by crystallisation from alcohol. 2-Nitrofluorene was added slowly to a mixture of equal volumes of glacial acetic and fuming nitric acids; a yellow solid

then separated consisting of almost pure 2 : 7-dinitrofluorene. The filtrate poured into water gave a precipitate from which 2-nitrofluorene was extracted with hot alcohol. The residue crystallised from glacial acetic acid consisted of 2 : 5-dinitrofluorene (m. p. 207°) identical with the product of direct nitration.

2 : 5-*Dinitrofluorenone.*—2 : 5-Dinitrofluorene dissolved in glacial acetic acid was heated under reflux with chromium trioxide for an hour. The crude ketone separated on cooling and was crystallised from glacial acetic acid, in which it was much less soluble than 2 : 5-dinitrofluorene. It separated in light yellow needles, m. p. 241° (Found : N, 10·55. $C_{13}H_6O_5N_2$ requires N, 10·6%).

2 : 7-*Dinitrofluorenone* was obtained from 2 : 7-dinitrofluorene as in the preceding oxidation, and crystallised from the same solvent in bright yellow needles, m. p. 290°, identical with the dinitroketone obtained from 2 : 7-dinitrophenanthraquinone (Schmidt and Bauer, *Ber.*, 1905, **38**, 3744). This dinitrofluorenone was also identified by conversion into its oxime (m. p. 285—286°; *loc cit.*).

2 : 7-*Diaminofluorene.*—The dinitro-compound was reduced to the diamine either by tin and hydrochloric acid or by sodium hyposulphite (" hydros ").

In the former case, tin, hydrochloric acid, and some platinum foil were added to a suspension of the dinitro-compound in alcohol, and the mixture was heated under reflux until the yellow solid had disappeared. On cooling, a colourless, crystalline stannichloride separated; this, on treatment with sodium hydroxide, liberated the diamine, which was extracted with ether. If a large excess of alcohol was used, the stannichloride remained dissolved; the solution, rendered alkaline with sodium hydroxide, was extracted with benzene to remove the diamine. From ether or benzene, the diamine crystallised in colourless plates, m. p. 165°.

In the " hydros " reduction, 50 g. of sodium hyposulphite were added gradually to 5·4 g. of 2 : 7-dinitrofluorene suspended in 250 c.c. of alcohol diluted with an equal volume of water, the mixture being heated under reflux until the liquor, which reddened at first, became colourless. The alcohol was removed by distillation, and the residue boiled with 100 c.c. of concentrated hydrochloric acid and 100 c.c. of water. The solution was filtered, and the residual solid again boiled repeatedly with dilute acid. The filtrates were combined, cooled with ice, and rendered ammoniacal. The black precipitate was collected and extracted with benzene, and the base was obtained from this solvent in colourless plates which dissolved readily in alcohol or chloroform and developed an olive-green coloration with ferric chloride.

Acetylation of 2 : 7-*Diaminofluorene.*—2 : 7-Diaminofluorene was

dissolved in hot acetic anhydride; the solution, on cooling in ice, yielded *diacetyl-2 : 7-diaminofluorene* as a colourless, crystalline solid which dissolved sparingly in benzene or carbon tetrachloride and separated from the former solvent in colourless, glistening plates, m. p. 281° (Found : N, 10·2. $C_{17}H_{16}O_2N_2$ requires N, 10·0%).

On being poured into water, the acetic anhydride filtrate yielded other acetyl derivatives, which were separated by fractional crystallisation from benzene. The less soluble *triacetyl-2 : 7-diaminofluorene* separated in colourless needles, m. p. 234° (Found : N, 8·5. $C_{19}H_{18}O_3N_2$ requires N, 8·7%). The more soluble *tetra-acetyl-2 : 7-diaminofluorene* crystallised from petroleum (b. p. 80—120°) in colourless, iridescent needles, m. p. 179—181° (Found : N, 7·7. $C_{21}H_{20}O_4N_2$ requires N, 7·7%).

The lowering of melting point with the increase of acetyl groups is comparable with the changes of fusibility recorded for the acetyl derivatives of benzidine.

On boiling 2 : 7-diaminofluorene with glacial acetic acid, the main product was diacetyl-2 : 7-diaminofluorene. By heating the diamine with excess of 90% formic acid, a formyl derivative was obtained which separated in glistening, lath-like crystals, m. p. 272°.

2 : 5-*Diaminofluorene*.—The reduction of 2 : 5-dinitrofluorene was made with hyposulphite and with tin and hydrochloric acid, the former process giving the purer product.

To 2 g. of the dinitro-compound in 600 c.c. of alcohol and 100 c.c. of hot water were slowly added 20 g. of sodium hyposulphite, the mixture being boiled until the red colour had disappeared. The solution was then treated as in the case of 2 : 7-diaminofluorene. The benzene extract yielded pinkish-white needles, m. p. 175°, which dissolved in alcohol and developed an olive-green coloration with ferric chloride (Found : N, 13·9. $C_{13}H_{12}N_2$ requires N, 14·3%).

The reduction with tin and hydrochloric acid was effected as in the case of the isomeric diamine. The new diamine obtained by ether extraction was accompanied by a tarry impurity which also had basic properties.

Diacetyl-2 : 5-diaminofluorene, obtained by heating the diamine with glacial acetic acid, crystallised from methyl alcohol in colourless, transparent, six-sided prisms, m. p. 289° (Found : N, 10·5. $C_{17}H_{16}O_2N_2$ requires N, 10·0%).

Production of 2 : 5-Dinitrofluorenone from Phenanthraquinone.—Phenanthraquinone nitrated by Schmidt and Austin's method (*Ber.*, 1903, **36**, 3731) yielded 2- and 4-nitrophenanthraquinones, which were separated by fractional crystallisation from glacial acetic acid,

in which the 2-nitro-compound was only sparingly soluble. The more soluble 4-nitrophenanthraquinone (IV) was crystallised from alcohol and converted into 4-nitrodiphenyleneglycollic acid (V) by warming 3·5 g. with 350 c.c. of 10% potassium hydroxide solution for 20 minutes at 65° (Schmidt and Bauer, *Ber.*, 1905, **38**, 3741). The purified 4-nitrodiphenyleneglycollic acid (23 g.) was boiled with 350 c.c. of water, and the solution concentrated to 150 c.c. A mixture of two compounds separated (Schmidt and Bauer, *loc. cit.*); 4-nitrofluorenone (VI) was isolated from this by means of its much greater solubility in glacial acetic acid, and purified by crystallisation from alcohol.

To 4-nitrofluorenone, dissolved in glacial acetic acid, an equal volume of fuming nitric acid was added and the mixture was brought to the boiling point and maintained at 100° for 20 minutes. The nitration mixture was poured into water, and the yellow product crystallised from glacial acetic acid; long, yellow needles of 2 : 5-dinitrofluorenone (III), m. p. 241°, were thus obtained. This preparation did not depress the melting point of the ketone obtained on oxidising 2 : 5-dinitrofluorene.

The authors desire to express their thanks to Messrs. Hardman and Holden for the specimen of fluorene used in this investigation.

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[*Received, September 3rd,* 1926.]

CCCLVI.—*Phototropic Amino-aryl Disulphoxides.*

By REGINALD CHILD and SAMUEL SMILES.

IN a previous communication (J., 1924, **125**, 2359), it was shown that acetanilide *p*-disulphoxide (I) is phototropic, but examination of the material then available did not reveal the existence of other disulphoxides endowed with this property. Use has now been made of the various methods of synthesising disulphoxides in the exploration of this group, with the result that further information is available concerning the structural and physical conditions which determine the phototropic character. The orientation of the amino-groups is of importance; thus, whilst aniline and acetanilide *p*-disulphoxides may be obtained in the phototropic state, the property has not been observed with the *o*- and *m*-derivatives. Introduction of hydrocarbon groups in the aromatic nuclei of acetanilide *p*-disulphoxide does not profoundly influence the phototropic character, 1-*acetylaminonaphthyl* 4-*disulphoxide* (II) and

2-acetylaminotolyl 5-disulphoxide (as III) * having both been isolated as phototropic materials.

$NHAc \quad NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NHAc \quad NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_6H_4Me$
(I.) (IV.)

Me

S–
(III.)

$NHAc{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}S{\cdot}C_{10}H_6{\cdot}NHAc \quad C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NHAc$
(II.) (V.)

Acylation of the amino-groups in aniline *p*-disulphoxide diminishes the sensitiveness of the material and may obliterate the phototropic character. The diacetyl derivative is less sensitive than the parent substance, but the *dicarbethoxy-* and the *dicarbomethoxy*-compounds appear to be devoid of phototropic character. Finally, two unsymmetrical disulphoxides containing one *p*-acetylamino-group have been examined, *viz.*, p-*tolyl* p-*acetylaminobenzenethiolsulphonate* (IV) and p-*acetylaminophenyl* p-*chlorobenzenethiolsulphonate* (V). Only the latter is phototropic, hence it seems that the presence of one amino-group in the thiol-substituted nucleus is sufficient to evoke the property. Other substances related to acetanilide disulphoxide have been examined, and among these *acetanilide* p-*disulphone* (VI) and p-*acetylaminophenyl* p-*acetylaminobenzenesulphonate* (VII) are not phototropic.

$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}NHAc \quad NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}NHAc$
(VI.) (VII.)

Of greater interest than these structural conditions attending the property is the fact that after thorough purification neither acetanilide *p*-disulphoxide nor aniline *p*-disulphoxide is phototropic; but when a pure inactive sample of either of these disulphoxides is mixed with a small quantity—about 0·1%—of the corresponding disulphide the material becomes phototropic, and with larger amounts of the disulphide—up to about 5%—the product acquires a permanent deep yellow colour. By no means all disulphides stimulate acetanilide *p*-disulphoxide in this manner; the effect appears to be confined to those disulphides containing the 4-amino- or substituted 4-amino-phenyl group, and it is remarkable that the 3-acetylamino- and 2-acetylamino-phenyl disulphides are without influence either on the corresponding disulphoxides or on the

* This derivative of *o*-toluidine was obtained by converting the corresponding sulphonic acid (Nevile and Winther, *Ber.*, 1880, **13**, 1941) into the disulphide and oxidising this with hydrogen peroxide. The disulphide, of which the orientation is thus known, is identical with the disulphide obtained by Hodgson (J., 1912, **101**, 1700) from the product of interaction of sulphur and *o*-toluidine hydrochloride at a high temperature. The constitution of this material has hitherto been uncertain.

4-acetylamino-phenyl isomeride. No theoretical interpretation of these facts is offered at present, but the relation between the phototropy of these disulphoxides and the presence of small quantities of the reduction products accords with the opinion of Stobbe (*Annalen*, 1908, **359**, 1) that phototropic change is accompanied by chemical change in the material. Moreover it is evident that support is forthcoming in aid of the opinion expressed by Gallagher (*Bull. Soc. chim.*, 1921, **29**, 961), who has claimed on other grounds a close connexion between the phenomena of phosphorescence and phototropy.

Experimental.

Aniline p-*Disulphoxide*.—Recrystallised acetanilide-*p*-disulphoxide, prepared from hydrogen iodide and acetanilide-*p*-sulphinic acid, was hydrolysed with boiling hydrochloric acid, and the diluted solution made weakly acid (to thymol-blue) by addition of sodium carbonate. The precipitate was repeatedly crystallised from acetone with the aid of charcoal. The product formed colourless leaflets, m. p. 183° (Found : N, 10·2; S, 23·0. Calc. : N, 10·0; S, 22·9%). The material described (J., 1924, **125**, 2361) as yellow (m. p. 175°) contained disulphide. A pure inactive sample of acetanilide *p*-disulphoxide obtained by treating the purified base with acetic anhydride was colourless and had m. p. 236—237° (decomp.). These substances cannot be purified by means of hot alcohol (compare Hinsberg, *Ber.*, 1909, **42**, 1278), since this solvent generates the disulphides by reduction.

The influence of disulphides on the properties of these and other disulphoxides was investigated by adding excess of water to cold acetic acid or acetone solutions containing measured quantities of the substances. Since these are insoluble in water, the required mixtures separated in the crystalline state. Mere admixture of the solid materials is not sufficient to induce phototropy and it is probable that the formation of mixed crystals is necessary to these phenomena of stimulation.

Dicarbomethoxyaminodiphenyl p-*disulphoxide*, $S_2O_2(C_6H_4{\cdot}NH{\cdot}CO_2Me)_2$, was obtained by boiling a solution of the crude base in acetone for ½ hour with methyl chloroformate and sodium carbonate. After purification it formed colourless needles, m. p. 186° (Found : C, 48·7; H, 4·3. $C_{16}H_{16}O_6N_2S_2$ requires C, 48·4; H, 4·0%). The *dicarbethoxy*-compound, $S_2O_2(C_6H_4{\cdot}NH{\cdot}CO_2Et)_2$, prepared in a similar manner, formed leaflets, m. p. 162° (Found : C, 50·7; H, 4·9; N, 6·8. $C_{18}H_{20}O_6N_2S_2$ requires C, 50·9; H, 4·7; N, 6·6%).

Dicarbethoxyaminodiphenyl p-*disulphide*, $S_2(C_6H_4{\cdot}NH{\cdot}CO_2Et)_2$,

forms prisms, m. p. 136—137°, from alcohol (Found: C, 54·9; H, 5·2. $C_{18}H_{20}O_4N_2S_2$ requires C, 55·1; H, 5·1%).

p-*Acetylaminophenylmethylsulphone*, $NHAc{\cdot}C_6H_4{\cdot}SO_2Me$, prepared by methylation of the sulphinic acid, separated from hot water in needles, m. p. 183° (Found: N, 6·7. $C_9H_{11}O_3NS$ requires N, 6·5%).

Acetanilide p-*Disulphone* (VI).—Potassium permanganate (0·8 g.) was gradually added to a cooled, stirred solution of acetanilide-*p*-sulphinic acid (6 g.) in acetic acid (80 c.c.). The required material (1·2 g.), isolated after the addition of excess of sulphurous acid, was colourless, almost insoluble in the usual solvents, and had m. p. 245—250° (decomp.) (Found: C, 48·6; H, 4·4. $C_{16}H_{16}O_6N_2S_2$ requires C, 48·4; H, 4·1%). No evidence of phototropic properties of these sulphones and urethanes could be obtained.

p-*Acetylaminophenyl* p-*Acetylaminobenzenesulphonate* (VII).—A mixture of *p*-acetylaminobenzenesulphonyl chloride (4·6 g.), *p*-acetylaminophenol (3 g.), and dry pyridine (2 g.) was kept at 100° for ½ hour. The desired substance (3 g.) was isolated by treating the product with dilute sulphuric acid. Purified from alcohol, it had m. p. 218° (Found: C, 55·0; H, 4·8; S, 9·2. $C_{16}H_{16}O_5N_2S$ requires C, 55·1; H, 4·6; S, 9·2%).

Acetanilide o-*Disulphoxide*.—Aniline *o*-disulphide (Mohlau, *Ber.*, 1912, **45**, 134) was converted into the *diacetyl* derivative, which separated from dilute acetic acid in needles, m. p. 156° (Found: C, 57·6; H, 5·0. $C_{16}H_{16}O_2N_2S_2$ requires C, 57·8; H, 4·8%). A solution of this substance (2·8 g.) in acetic acid (28 c.c.) containing hydrogen peroxide (2 c.c. of 30% solution) was kept for 4 days and then added to water (150 c.c.). The material which separated crystallised from dilute acetic acid (charcoal) in colourless plates (1·5 g.), m. p. 140° (Found: C, 52·5; H, 4·5; N, 7·8. $C_{16}H_{16}O_4N_2S_2$ requires C, 52·7; H, 4·5; N, 7·7%). Poorer yields of the disulphoxide were obtained when larger quantities of material were used. The substance was not phototropic and was not stimulated when mixed with the corresponding disulphide.

Acetanilide-m-*sulphinic Acid*.—Finely-divided acetanilide-*m*-sulphonyl chloride was treated with an excess of sodium sulphite in aqueous alkaline solution until it dissolved. The required sulphinic acid (60% yield) was liberated by addition of sulphuric acid; after crystallisation from hot water, it had m. p. 145° (Found: N, 7·1. $C_8H_9O_3NS$ requires N, 7·0%).

When a solution of this sulphinic acid (20 g.) in water (800 c.c.) containing a few drops of hydriodic acid and an excess of sulphurous acid was kept at 90° for 2—3 hours, *acetanilide* m-*disulphoxide* was precipitated (30% yield). Crystallised from dilute acetic acid with

the aid of charcoal, this substance was obtained colourless and had m. p. 212—213° (decomp.). It was not sensitive to light either in the pure condition or when mixed with the disulphide (Found : C, 52·3; H, 4·9; N, 7·7. $C_{16}H_{16}O_4N_2S_2$ requires C, 52·7; H, 4·5; N, 7·7%).

2-*Acetylaminotoluene-5-sulphonyl Chloride* (formula as III).—Thoroughly dried sodium 2-acetylaminotoluene-5-sulphonate (20 g.), which had been obtained from the aminosulphonate by treatment with acetic anhydride, was triturated with phosphorus pentachloride (20 g.) until the liquid material had solidified. After 1 hour, the product was treated in the usual manner; the dried sulphonyl chloride (16 g.) crystallised from benzene in needles, m. p. 159°, which were soluble in the usual media (Found : C, 43·3; H, 4·3; Cl, 14·4; S, 12·9. $C_9H_{10}O_3NClS$ requires C, 43·6; H, 4·1; Cl, 14·4; S, 12·9%).

2-*Acetylaminotoluene-5-sulphinic Acid*, $NHAc{\cdot}C_6H_3Me{\cdot}SO_2H$.—The sulphonyl chloride (18 g.) was shaken with an aqueous alkaline solution (100 c.c.) of sodium sulphite (50 g.), and dilute sulphuric acid (60%) added to the solution obtained. The *sulphinic acid* (70% yield), which separated crystalline, after recrystallisation from hot water, had m. p. 147° (Found : N, 6·6. $C_9H_{11}O_3NS$ requires N, 6·6%).

Attempts to convert this acid into the disulphoxide by means of dilute hydriodic and sulphurous acids failed, the only product isolated being a small quantity of the disulphide. 2-*Acetylaminotolyl 5-mercaptan*, $NHAc{\cdot}C_6H_3Me{\cdot}SH$, prepared by reducing an alcoholic solution of the sulphonyl chloride with zinc and hydrochloric acid (compare Zincke, *Ber.*, 1909, **42**, 3367), formed needles, m. p. 143°, from aqueous alcohol (Found : C, 59·6; H, 6·5; S, 17·5. $C_9H_{11}ONS$ requires C, 59·6; H, 6·1; S, 17·7%). 2-*Acetylamino-5-tolyl methyl sulphide*, $NHAc{\cdot}C_6H_3Me{\cdot}SMe$, obtained from the mercaptan and methyl sulphate, had m. p. 134° (Found : C, 61·2; H, 6·7. $C_{10}H_{13}ONS$ requires C, 61·4; H, 6·7%). Oxidation of the mercaptan in alcoholic solution with ferric chloride yielded 2-*acetylaminotolyl 5-disulphide*, $(S{\cdot}C_6H_3Me{\cdot}NHAc)_2$, which separated from acetic acid in leaflets, m. p. 222° (Found : C, 59·9; H, 5·2. $C_{18}H_{20}O_2N_2S_2$ requires C, 59·9; H, 5·5%). On hydrolysis with concentrated hydrochloric acid this substance was converted into 2-*aminotolyl 5-disulphide* (Found : C, 60·3; H, 5·6. $C_{14}H_{11}N_2S_2$ requires C, 60·8; H, 5·8%), which, after purification by means of aqueous alcohol, had m. p. 112°. This substance and its acetyl derivative were identified in the usual manner with the corresponding materials prepared from *o*-toluidine hydrochloride and sulphur by Hodgson's method (*loc. cit.*).

2-Acetylaminotolyl 5-disulphoxide (as III) was obtained by the action of hydrogen peroxide (30% solution) on a mixture of the disulphide and acetic acid (20 parts). After 8 days, the solution was treated with water and the material which separated was purified in the usual manner. The substance, m. p. 183° (decomp.), separated from hot alcohol in yellow needles (Found: C, 54·9; H, 5·3. $C_{18}H_{20}O_4N_2S_2$ requires C, 55·1; H, 5·1%). This colour was undoubtedly due to the presence of a small quantity of the disulphide, but sufficient material was not available for treatment by the method applied to the acetanilide derivative.

1-Acetylaminonaphthalene-4-sulphinic Acid, $NHAc{\cdot}C_{10}H_6{\cdot}SO_2H$. —1-Acetylaminonaphthalene-4-sulphonyl chloride (Schroeter, *Ber.*, 1906, **39**, 1559; Zincke and Schutz, *Ber.*, 1912, **45**, 473) (30 g.) was shaken with sodium sulphite (110 g.) and water (200 g.) until it dissolved. The required *acid* was isolated in the usual manner; after crystallisation from dilute alcohol, it had m. p. 176° (decomp.) (Found: C, 57·6; H, 4·2. $C_{12}H_{11}O_3NS$ requires C, 57·8; H, 4·4%).

1-Acetylaminonaphthyl 4-disulphoxide (III) was obtained (25% yield) from the sulphinic acid by treatment in aqueous alcohol with sulphurous and hydriodic acids in the usual manner. The *disulphoxide*, which separated very slowly, was collected at intervals to avoid the inclusion of a more soluble blue material which was simultaneously formed (compare Reissert, *Ber.*, 1922, **55**, 858). It crystallised from acetic acid in pale yellow needles, m. p. 234° (decomp.) (Found: C, 61·8; H, 4·6. $C_{24}H_{20}O_4N_2S_2$ requires C, 62·0; H, 4·3%). It is probable that the substance contained a trace of the disulphide. The orange tint developed by exposing the material to sunlight was rapidly destroyed at 100°. Proof that the substance contains the disulphoxide structure was obtained by the action of 2 : 5-dibromophenyl mercaptan (compare Gibson and Smiles, J., 1924, **125**, 178), 1-acetylaminonaphthalene-4-sulphinic acid and the following unsymmetrical disulphide being produced.

2 : 5-*Dibromophenyl 4-acetylaminonaphthyl disulphide*,

$$NHAc{\cdot}C_{10}H_6{\cdot}S{\cdot}S{\cdot}C_6H_3Br_2,$$

separates from alcohol in colourless needles, m. p. 189° (Found: Br, 33·2. $C_{18}H_{13}ONBr_2S_2$ requires Br, 33·1%).

Acetanilide-p-sulphonyl iodide, $NHAc{\cdot}C_6H_4{\cdot}SO_2I$, was prepared by adding the requisite amount of iodine, dissolved in alcohol, to a dilute aqueous solution of sodium acetanilide-*p*-sulphinate. It was purified by the addition of light petroleum to an ethereal solution and formed yellow needles, m. p. 97° (decomp.) (Found: I, 39·1. $C_8H_6O_3NIS$ requires I, 39·0%).

p-*Tolyl* p-*acetylaminobenzenethiolsulphonate* (IV) was obtained (10% yield) by the interaction of silver *p*-tolyl mercaptide and acetanilide-*p*-sulphonyl iodide in presence of dry ether (compare Miller and Smiles, J., 1925, **127**, 229). The soluble *p*-tolyl disulphide also formed was readily separated from the required *disulphoxide*, this being sparingly soluble in alcohol. It was colourless, had m. p. 169° (decomp.), and was not phototropic (Found: C, 56·1; H, 4·6. $C_{15}H_{15}O_3NS_2$ requires C, 56·0; H, 4·7%).

p-*Acetylaminophenyl* p-*Chlorobenzenethiolsulphonate* (V).—When the requisite amount of bromine was added to acetanilide *p*-disulphide (m. p. 215°) suspended in carbon tetrachloride, an orange, crystalline material was formed. This was evidently acetanilide *p*-sulphur bromide, since it was converted by alcohol and similar agents into the original disulphide, but it was not sufficiently stable to permit isolation for analysis. This material was triturated with an excess of silver *p*-chlorobenzenesulphinate in presence of carbon tetrachloride. The insoluble portion was collected and treated with alcohol, which dissolved the required disulphoxide and acetanilide disulphide. These were separated in the usual manner. The unsymmetrical *disulphoxide* was obtained in colourless needles, m. p. 200—201° (decomp.), which became yellow on brief exposure to sunlight; the colour disappeared when the sample was kept in the dark (Found: C, 49·0; H, 3·3. $C_{14}H_{12}O_3NClS_2$ requires C, 49·1; H, 3·5%).

KING'S COLLEGE, LONDON. [*Received, June 13th*, 1926.]

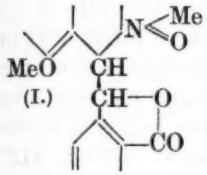
CCCLVII.—*The Oxidation of Narcotine by Hydrogen Peroxide.*

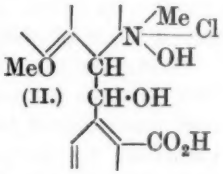
By ALLAN MACLEAN DRUMMOND and ANDREW MCMILLAN.

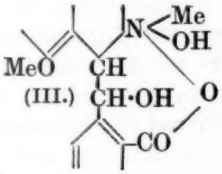
THE formation of amine oxides by the action of hydrogen peroxide on alkaloids containing a nitrogen atom linked to three different carbon atoms is now well established. Pictet (*Ber.*, 1905, **38**, 2786) states that this nitrogen-linking is essential to the production of such substances (compare, however, Meisenheimer, *Ber.*, 1925, **58**, 2334). Amine oxides have been prepared from strychnine, brucine, quinine, and morphine (Pictet and Mathieson, *Ber.*, 1905, **38**, 2782; Freund and Speyer, *Ber.*, 1910, **43**, 3310; Speyer and Becker, *Ber.*, 1922, **55**, 1321). Among these, differences in the reactivity of the amine-oxidic oxygen atoms are found, as shown by their action on aqueous potassium iodide.

The oxidation of *l*-narcotine with hydrogen peroxide involved

considerable difficulty and only when the conditions described below were rigidly followed was a crystalline product, $C_{22}H_{23}O_8N$, m. p. 229°, obtained. This substance, which we represent as *narcotine oxide* (I), is feebly basic and optically active, being dextrorotatory. From its insolubility in aqueous sodium carbonate it appears that the lactonic structure, which is present in narcotine, is unaffected, as otherwise a carboxyl group would undoubtedly be produced. Whilst oxidation of narcotine by other means has resulted in the fission of the molecule between the *iso*quinoline and benzenoid nuclei, with hydrogen peroxide the complexity of the molecule is preserved. Oxidation of the amine oxide with nitric acid yielded hemipinic acid.







With concentrated hydrochloric acid, narcotine oxide yielded a crystalline *hydrochloride* (II), $C_{22}H_{25}O_9N,HCl$, m. p. 191°. The formation of this substance must be accompanied by some change such as the rupture of the lactone ring, as the hydrochloride contains a carboxyl group. It is readily hydrolysed to an optically inactive *acid*, $C_{22}H_{25}O_9N$, m. p. 212°, and reconversion into the hydrochloride is easily effected. The stability of this substance as a hydroxy-acid appears remarkable, but a parallel is found in the case of the hydroxy-acid from gnoscopine. Rabe and McMillan (*Annalen*, 1910, **377**, 242) have shown this substance to be much more stable than the corresponding compound from narcotine. The stability of the former is probably due to its greater insolubility. We suggest that the amine hydroxy-acid may be a betaine (III).

Experimental.

Oxidation of Narcotine by Hydrogen Peroxide.—To 20 g. of *l*-narcotine (1 mol.), dissolved in 50 c.c. of glacial acetic acid, were added in the cold, at the rate of 1 c.c. per day, 12 c.c. of 30% aqueous hydrogen peroxide (2 mols.). The yellow liquid was almost neutralised with sodium carbonate, sufficient acid being left to retain any unchanged narcotine in solution; and the sticky mass, which separated, was extracted with chloroform. From this extract, after shaking with sodium carbonate followed by water to remove acidity, a viscous material was obtained which, when stirred with 150 c.c. of dry acetone and cooled in ice, left a yellow solid (5 g.).

This substance, presumably *narcotine oxide*, separated from hot acetone in small, white needles, m. p. 229°, $[\alpha]_D$ + 139° for a 3% solution in chloroform (Found: C, 61·2; H, 5·2; N, 3·1. $C_{22}H_{23}O_8N$ requires C, 61·1; H, 5·4; N, 3·3%).

This compound does not liberate iodine from aqueous potassium iodide and is unaffected by the usual reducing agents (sulphur dioxide in chloroform solution or alkaline sodium sulphite). It is only sparingly soluble in the ordinary organic solvents, readily soluble in concentrated acids, and is unaffected by alkali. It has no marked physiological properties, which is in agreement with the recent results obtained by Polonovski (*Compt. rend.*, 1925, **181**, 887) in connexion with other alkaloidal *N*-oxides.

Oxidation of Narcotine Oxide with Nitric Acid.—The oxide (3 g.) was treated with a solution of 8 c.c. of concentrated nitric acid in 30 c.c. of water at 50°. Oxidation was slow on account of the sparing solubility, and after 14 days the unchanged material was filtered off. Hemipinic acid was isolated from the nearly neutralised solution, and was identified by its equivalent (found, 112; calc., 113), m. p., and mixed m. p. with an authentic specimen (177°).

Action of Hydrochloric Acid on Narcotine Oxide.—The oxide, dissolved in chloroform, was unaffected by hydrogen chloride; but from a solution of 5 g. of the oxide in 100 c.c. of concentrated hydrochloric acid a solid began to separate after 24 hours, and the amount increased on addition of water. This substance readily crystallised (m. p. 191°) from absolute alcohol and was soluble in aqueous sodium carbonate (Found: C, 55·0; H, 5·5; Cl, 7·1. $C_{22}H_{25}O_9N$,HCl requires C, 54·7; H, 5·4; Cl, 7·3%). It is regarded as the *hydrochloride* of the hydroxy-acid produced from narcotine oxide. It is stable in the presence of hydrochloric acid, but repeated crystallisation from aqueous alcohol or exposure to air gradually converts it into the *hydroxy-acid* itself, m. p. 212°, which is insoluble in all ordinary organic solvents. This change is accelerated by warming with water (Found: C, 58·8; H, 5·5; N, 3·3. $C_{22}H_{25}O_9N$ requires C, 59·1; H, 5·6; N, 3·1%).

Excess of concentrated hydrochloric acid was added to a solution of this acid in aqueous sodium hydroxide. A crystalline solid rapidly separated, and was identified as the hydrochloride, m. p. 191°.

The addition of lead acetate to a solution of the ammonium salt in water precipitated a yellow *lead* salt [Found: Pb, 18·2. $(C_{22}H_{24}O_9N)_2Pb$ requires Pb, 18·8%].

Dilute sulphuric acid precipitated from a solution of the sodium salt a viscous oil, which dissolved on being gently warmed. From

this solution there separated a *sulphate* in small, white needles, m. p. 148° [Found : SO_4, 9·1. $(C_{22}H_{25}O_9N)_2,H_2SO_4$ requires SO_4, 9·7%].

The authors desire to express their indebtedness to the Royal Society for a grant which enabled them to carry out this work.

UNIVERSITY OF GLASGOW. [*Received, July 14th,* 1926.]

CCCLVIII.—*Investigations in the Diphenyl Series. Part II. Substitution Reactions.*

By FRANK BELL and JOSEPH KENYON.

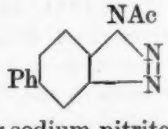
THE dinitration of diphenyl has been described by Fittig (*Annalen*, 1862, **124**, 276), Schultz (*Annalen*, 1874, **174**, 201), and Willstätter (*Ber.*, 1906, **39**, 3478), the products isolated being 4 : 4′- and 2 : 4′-dinitrodiphenyls. Schultz and Strasser (*Ber.*, 1881, **14**, 612) record that 2-nitrodiphenyl on re-nitration gives 2 : 4′-dinitrodiphenyl. The nitration of 4-nitrodiphenyl does not appear to have been described. It has now been found that both in the dinitration of diphenyl and in the nitration of 2-nitrodiphenyl there are also produced considerable quantities of 2 : 2′-dinitrodiphenyl; under similar conditions 4-nitrodiphenyl gives 2 : 4′- and 4 : 4′-dinitrodiphenyls. The non-formation of any considerable quantity of 2 : 4-dinitrodiphenyl in these various reactions is somewhat surprising.

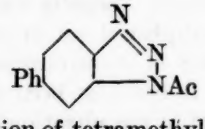
The isolable products of the nitration of 4-benzylideneaminodiphenyl in sulphuric acid solution are soluble in ammonia—an indication that simultaneous sulphonation has taken place. By using a smaller proportion of sulphuric acid a small yield of 4′-nitro-4-aminodiphenyl is obtained. This result is in marked contrast to the facile nitration of 4-acetylaminodiphenyl and of 4-dimethylaminodiphenyl, which give only the 3-nitro-derivatives (compare Fichter and Sulzberger, *Ber.*, 1904, **37**, 878; Garciá Banús and Ferrer Tomás, *Anal. Fís. Quím.*, 1921, **19**, 293). Since 4-hydroxydiphenyl on energetic nitration gives 3 : 5 : 4′-trinitro-4-hydroxydiphenyl (Garciá Banús and Guiteras, *Anal. Fís. Quím.*, 1923, **21**, 126) whilst 4-acetylaminodiphenyl on chlorination (bromination) gives 3 : 5 : 4′-trichloro(tribromo)-4-acetylaminodiphenyl (Scarborough and Waters, this vol., p. 557), the alleged conversion of 3-nitro-4-dimethylaminodiphenyl into 3 : 5 : 2′ : 4′-tetranitro-4-dimethylaminodiphenyl by further nitration (Garciá Banús and Ferrer Tomás, *loc. cit.*) seemed very striking. It has now been found that this product is a dinitro-4-nitrosomethylaminodiphenyl.

Its constitution has been confirmed by its preparation from 4-nitrosomethylaminodiphenyl.

Nitration of 3-nitro-4-dimethylaminodiphenyl in sulphuric acid solution gives a dinitro-derivative, m. p. 137—138°. This is probably identical with the dinitro-compound, m. p. 134°, believed by Vorländer (*Ber.*, 1925, **58**, 1909) to be 3 : 4′-dinitro-4-dimethylaminodiphenyl. Addition of one molecular proportion of nitric acid to a solution of 4-dimethylaminodiphenyl in sulphuric acid produces a mononitro-monosulphonic acid together with a small proportion of the dinitrated amine.

3 : 4-Diaminodiphenyl has been obtained in greatly improved yield and some of its derivatives have been examined. 3-Amino-4-acetylaminodiphenyl reacts with nitrous acid to give 1-*acetyl*-5-*phenyl*-1 : 2 : 3-*benztriazole* (I), which was also obtained together with 1-*acetyl*-6-*phenyl*-1 : 2 : 3-*benztriazole* (II) by the acetylation of 5 (or 6)-phenyl-1 : 2 : 3-benztriazole.

(I.) 



(II.)

On adding sodium nitrite to a solution of tetramethylbenzidine in hydrochloric acid Michler and Pattinson (*Ber.*, 1881, **14**, 2164) obtained a dinitro-derivative, m. p. 188°, which gave a diamine, m. p. 168°, on reduction. Garciá Banús and Ferrer Tomás (*loc. cit.*) had difficulty in repeating this experiment and even by an improved method obtained only a product of m. p. 181—183°. By replacing the hydrochloric acid by acetic acid we have obtained an almost quantitative yield of the dinitro-compound of m. p. 188°. Ullmann and Dieterle (*Ber.*, 1904, **37**, 23) prepared 2 : 2′-dinitrotetramethylbenzidine (m. p. 230°), by nitrating the amine in sulphuric acid solution, and from it the corresponding diamine, m. p. 166°. The two diamines are not identical, as has been shown by the melting point of a mixture of the two and by the properties of their diacetyl derivatives. 2-Nitrotetramethylbenzidine is converted by the action of sodium nitrite and acetic acid into a dinitro-derivative, m. p. 145°, which is almost certainly 2 : 3′-dinitrotetramethylbenzidine. It thus appears highly probable that Michler and Pattinson's dinitro-compound is 3 : 3′-dinitrotetramethylbenzidine. An attempt to synthesise this compound by Ullmann's method was unsuccessful, probably owing to the fact that these compounds decompose slightly above their melting points.

In continuation of the work recorded in Part I (this vol., p. 1239) the hydrolysis of 4-benzoyloxy-4′-acetylaminodiphenyl has been examined. The result is in complete agreement with that recently

published by Raiford and Clark (*J. Amer. Chem. Soc.*, 1926, **48**, 483)—4-hydroxy-4′-acetylaminodiphenyl is produced without any trace of 4-hydroxy-4′-benzoylaminodiphenyl. This result does not seem to be in harmony with the Kaufler formula for diphenyl, which, moreover, would require that mono-substituted derivatives such as 2-aminodiphenyl should be capable of exhibiting optical isomerism. No case of this kind is recorded in the literature and, as shown in the experimental part, the brucine and morphine salts of diphenyl-2-carboxylic acid have been repeatedly crystallised from various solvents without any indication of resolution being observed.

Experimental.

Nitration of Diphenyl.—Diphenyl (20 g.), dinitrated by Willstätter's method (*loc. cit.*), gave 4 : 4′-dinitrodiphenyl (6·7 g.) and a more soluble fraction (14·5 g.), m. p. 70—80°, which, after five recrystallisations from alcohol, gave pure 4 : 2′-dinitrodiphenyl. The solid obtained after evaporation of the alcoholic mother-liquors was crystallised four times from benzene, and the pure 2 : 2′-dinitrodiphenyl, m. p. 127—128°, thus obtained was compared with 2 : 2′-dinitrodiphenyl prepared from *o*-chloronitrobenzene by Ullmann's method (*Ber.*, 1901, **34**, 2177).

Nitration of 2-Nitrodiphenyl.—A mixture of 2-nitrodiphenyl (20 g.), fuming nitric acid (14 c.c.), and water (2 c.c.), having been gently warmed for ½ hour, was poured into water. The precipitated semi-solid material was filtered to remove unchanged 2-nitrodiphenyl (1·5 g.) and the residual solid (21 g.) was separated by the method described above into 4 : 2′- and 2 : 2′-dinitrodiphenyls.

Nitration of 4-Nitrodiphenyl.—4-Nitrodiphenyl (20 g.), after being nitrated and worked up by the procedure described above, gave 4 : 4′-dinitrodiphenyl (11·4 g.) and a more soluble product (11 g.) from which, after many recrystallisations, pure 4 : 2′-dinitrodiphenyl was isolated. *2′-Nitro-4-dimethylaminodiphenyl*, prepared by shaking together 2′-nitro-4-aminodiphenyl, methyl sulphate, and sodium hydroxide solution, crystallised from alcohol in small, crimson needles, m. p. 100° (Found : C, 69·6; H, 5·6. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%). The 2′-nitro-4-aminodiphenyl was obtained in poor yield by the action of ammonium sulphide on an alcoholic solution of 2′ : 4-dinitrodiphenyl.

4-Benzylideneaminodiphenyl was obtained, by the addition of benzaldehyde (1 mol.) to a boiling ethyl-alcoholic solution of 4-aminodiphenyl, in bulky, lustrous plates, m. p. 148° (Found : N, 5·55. $C_{19}H_{15}N$ requires N, 5·45%). To this compound (8·6 g.), suspended in sulphuric acid (13 c.c.), a mixture of nitric acid (3 c.c.) and sulphuric acid (2 c.c.) was added, and the liberated benzaldehyde

removed in a current of steam. The residual mixture was made alkaline, and the solid repeatedly crystallised from alcohol until the melting point became constant at 200° (4′-nitro-4-aminodiphenyl).

3-*Nitro*-4-p-*toluenesulphonylaminodiphenyl*.—4-*p*-Toluenesulphonylaminodiphenyl (6 g.) was warmed for 9 hours with a mixture of nitric acid (5 c.c.) and water (100 c.c.). The product (6·5 g.) crystallised from alcohol in long, yellow needles, m. p. 118° (rather indefinite) (Found : C, 62·0; H, 4·4. $C_{19}H_{16}O_4N_2S$ requires C, 61·9; H, 4·35%). By hydrolysis with 75% sulphuric acid at 100°, pure 3-nitro-4-aminodiphenyl was obtained.

3-*Nitro*-4-*acetylaminodiphenyl*. — 4′-Acetylaminodiphenyl was nitrated by Fichter and Sulzberger's method (*loc. cit.*). The crude product melted at 125—128° (yield, more than 90%). Crystallised from alcohol, in which it was completely soluble (thus indicating the absence of 3 : 5-dinitro-4-acetylaminodiphenyl), it gave pure 3-nitro-4-acetylaminodiphenyl, m. p. 132°; the mother-liquor contained 3-nitro-4-aminodiphenyl.

3 : 4-*Diaminodiphenyl* was prepared by adding aluminium amalgam to a suspension of 3-nitro-4-aminodiphenyl in moist ether until the red particles had disappeared. After removal of the aluminium hydroxide and evaporation of the ether, the residual diamine crystallised from alcohol in small, colourless cubes, m. p. 103° (yield, 70%) (Found : N, 14·9. Calc. : N, 15·2%).

Acetic anhydride converted the diamine into 3 : 4-*diacetyldiaminodiphenyl*, m. p. 163°. A solution of this compound in aqueous alcohol set to a thick, clear jelly which, after 24 hours, was completely transformed into compact, colourless needles (Found : N, 10·4. $C_{16}H_{16}O_2N_2$ requires N, 10·4%). The diamine was converted by benzoyl chloride and sodium hydroxide into 3 : 4-*dibenzoyldiaminodiphenyl*, which melted at 248° after being boiled with alcohol, in which it was almost insoluble (Found : N, 6·8. $C_{26}H_{20}O_2N_2$ requires N, 7·1%). 3 : 4-Diaminodiphenyl condensed with benzil in acetic acid solution to give the *quinoxaline* derivative, which separated from alcohol as a yellow, crystalline powder, m. p. 148° (Found : N, 7·9. $C_{26}H_{18}N_2$ requires N, 7·8%).

3-*Amino*-4-*acetylaminodiphenyl* was prepared by adding aluminium amalgam to a suspension of 3-nitro-4-acetylaminodiphenyl (25 g.) in moist ether (1·5 litres) until the yellow colour had disappeared. The ether was evaporated, and the residue extracted several times with boiling alcohol. The hot alcoholic extracts were concentrated, filtered, and cooled, the compound (17 g.) being then deposited in colourless platelets, m. p. 155° (Found : C, 74·5; H, 6·2. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2%). By the action of acetic anhydride and

of benzoyl chloride and sodium hydroxide it was converted into 3 : 4-diacetyldiamino- and 3 : 4-dibenzoyldiamino-diphenyl (described above) respectively. Benzoyl chloride reacted with a pyridine solution to give 3-*benzoylamino*-4-*acetylaminodiphenyl*, which separated as a white, crystalline powder, m. p. 186°, from alcohol (Found : N, 8·35. $C_{21}H_{18}O_2N_2$ requires N, 8·5%).

1-*Acetyl*-5-*phenyl*-1 : 2 : 3-*benztriazole* (I) was obtained by adding sodium nitrite (3·5 g.), dissolved in water, to a stirred solution of 3-amino-4-acetylaminodiphenyl (11·3 g.) in hydrochloric acid (12·5 c.c.) and water (300 c.c.). The dried precipitate separated from alcohol (300 c.c.) in fine, silky needles (6·4 g.), m. p. 130—132° (Found : Ac, 18·3. $C_{14}H_{11}ON_3$ requires Ac, 18·2%). 5 (or 6)-Phenyl-1 : 2 : 3-benztriazole (3·1 g.) was obtained from the alcoholic filtrate as a white, crystalline powder, m. p. 156° (Found : C, 73·4; H, 4·4; N, 21·1. Calc. : C, 73·8; H, 4·6; N, 21·8%). This triazole is readily soluble in sodium hydroxide solution and can be titrated with approximate accuracy, thymolphthalein being used as indicator (Found : *M*, 199. Calc. : *M*, 195).

By the action of acetic anhydride or acetyl chloride on its solution in pyridine it gives a mixture of the two possible acetyl derivatives (I and II) which, on account of their similar solubility, are difficult to separate, and it is not certain that (II) has been obtained pure. They each form needles, (I) m. p. 130—132°, (II) m. p. 97°. On heating (I) with acetic anhydride a mixture of (I) and (II), m. p. 92—97°, is obtained. The great stability of the linking of two of the three nitrogen atoms present in the molecules of these compounds is shown by the results of the estimation of nitrogen by Kjeldahl's method [Found : (I) N, 5·9, 6·0; (II) N, 5·9. $C_{14}H_{11}N_3$ requires N, 17·7 (= 3 × 5·9%). Found for 5 (or 6)-phenyl-1 : 2 : 3-benztriazole : N, 7·0, 7·1, 7·1. Calc. : N, 21·5 (= 3 × 7·16%)].

3-*Amino*-4-*benzoylaminodiphenyl*, prepared by the reduction of 3-nitro-4-benzoylaminodiphenyl with aluminium amalgam (compare preparation of 3-amino-4-acetylaminodiphenyl), melts at 221° (Found : N, 9·6. $C_{19}H_{16}ON_2$ requires N, 9·7%). It is difficultly soluble in acids and only moderately easily soluble in boiling alcohol. It reacts with acetic anhydride to give 3-*acetylamino*-4-*benzoylaminodiphenyl*, which crystallises from alcohol as a white powder, m. p. 211° (Found : N, 8·5. $C_{21}H_{18}O_2N_2$ requires N, 8·5%), and with benzoyl chloride and sodium hydroxide to give 3 : 4-dibenzoyldiaminodiphenyl (above).

4-*Dimethylaminodiphenyl*, prepared by shaking 4-aminodiphenyl with methyl sulphate and sodium hydroxide, crystallises from alcohol in lustrous, white plates, m. p. 123°. Diphenylyltrimethylammonium hydroxide, which is formed in considerable quantity

during the reaction, is best isolated as the bromide, m. p. 222°, by the addition of potassium bromide to the filtrate (Vorländer, *loc. cit.*).

When 4-aminodiphenyl is heated under reflux with sodium carbonate and methyl iodide (1 mol.), a considerable quantity of 4-dimethylaminodiphenyl methiodide, m. p. 218° (decomp.), is formed, so that this method possesses no advantage over the preceding one when the tertiary base is required.

3-*Nitro*-4-*dimethylaminodiphenyl*.—An excess of a solution of sodium nitrite was added to 4-dimethylaminodiphenyl (16·5 g.) in acetic acid, and the red crystals which gradually separated were recrystallised from methyl alcohol; they then melted at 74° (14·5 g.). Dilution of the acetic acid filtrate with water gave a further crop of the same crystals. On the other hand, the continued addition of sodium nitrite gave pale yellow crystals, m. p. 122° (compare below).

3-Nitro-4-dimethylaminodiphenyl does not combine with methyl iodide even at 100° in a sealed tube. Reduction of an ethereal solution by aluminium amalgam gave only crude 3-amino-4-dimethylaminodiphenyl, which was very difficult to purify. On warming this crude product with acetic anhydride, 3-*acetylamino*-4-*dimethylaminodiphenyl* was obtained which crystallised readily from alcohol in felted needles, m. p. 167° (Found : C, 75·5; H, 7·0. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·1%). 5-Phenyl-1 : 2-dimethylbenziminazole was not produced when this compound was boiled with acetic anhydride (compare Pinnow, *Ber.*, 1899, **32**, 1666).

3 : (5 ?)-*Dinitro*-4-*nitrosomethylaminodiphenyl*.—(a) Fuming nitric acid (5 c.c.) was added to 3-nitro-4-dimethylaminodiphenyl (9·6 g.), dissolved in warm acetic acid (60 c.c.), and after ½ hour the mixture was allowed to cool; pale yellow needles, m. p. 122°, were then obtained. The mother-liquor was poured into water, and the precipitate thus formed was crystallised from alcohol; after separation of a small amount of difficultly soluble material (m. p. 290—292°), a further crop of *dinitro*-4-*nitrosomethylaminodiphenyl* was obtained (Found : C, 51·9; H, 3·5; N, 18·6. $C_{13}H_{10}O_5N_4$ requires C, 51·7; H, 3·3; N, 18·5%).

(b) To 4-nitrosomethylaminodiphenyl (3 g.), dissolved in warm acetic acid (20 c.c.), fuming nitric acid (2 c.c.) was added. On cooling, lustrous needles, m. p. 122°, separated, identical with the product obtained by method (a).

3 : (5 ?)-*Dinitro*-4-*methylaminodiphenyl*.—Dinitro-4-nitrosomethylaminodiphenyl (4·5 g.) was heated under reflux with alcoholic hydrogen chloride (100 c.c.). The bright red needles thus obtained in theoretical yield melted at 142—143° after being boiled with

alcohol (Found: C, 57·3; H, 4·2. $C_{13}H_{11}O_4N_3$ requires C, 57·1; H, 4·0%). The substance was unchanged after boiling with acetic anhydride for 1 hour (compare Kauffmann, *Ber.*, 1907, **40**, 4006), but in warm acetic acid was rapidly reconverted into the nitroso-derivative on addition of sodium nitrite.

3 : (4′ ?)-*Dinitro*-4-*dimethylaminodiphenyl*. — 3-Nitro-4-dimethylaminodiphenyl (2·42 g.) was dissolved in sulphuric acid (40 c.c.), and nitric acid (3·8 c.c.) added drop by drop. After 3 hours, the mixture was poured on to ice, the product neutralised with ammonia, and the precipitate crystallised several times from alcohol, orange-red plates, m. p. 137—138°, being obtained (Found: C, 58·5; H, 4·3. $C_{14}H_{13}O_4N_3$ requires C, 58·6; H, 4·5%).

Nitration of 4-*Dimethylaminodiphenyl in Sulphuric Acid Solution*. —The nitration (4-dimethylaminodiphenyl, 2·7 g.; sulphuric acid, 20 c.c.; nitric acid, 1·1 c.c.) and the subsequent treatment were as described above. The pasty precipitate was separated from the alkaline liquid, dried, and extracted with benzene, which removed a very small quantity of a deep red, crystalline compound [probably 2 : 4′(?)-dinitro-4-dimethylaminodiphenyl], m. p. 170—171° (Found: C, 58·7; H, 4·7. $C_{14}H_{13}O_4N_3$ requires C, 58·6; H, 4·5%). The part insoluble in benzene crystallised from alcohol in orange plates, m. p. 215—217°, which contained sulphur and evolved ammonia when heated with dilute alkali (Found: C, 49·1; H, 4·8. $C_{14}H_{17}O_5N_3S$ requires C, 49·5; H, 5·0%). This compound dissolved in warm dilute hydrochloric acid, and, on cooling, long, colourless needles separated which did not melt at 300°. Owing to the explosive character of this derivative, analysis by combustion proved useless. The yield of dinitro-4-dimethylaminodiphenyl was not increased by the use of 2 mols. of nitric acid in its preparation.

2 : 2′-*Diaminotetramethylbenzidine*, prepared by Ullmann and Dieterle's method (*loc. cit.*), crystallised from alcohol in plates, m. p. 166°. With acetic anhydride, it yielded the *diacetyl* derivative, which crystallised in fine, white leaflets, m. p. 191—192°, from aqueous alcohol (Found: C, 67·6; H, 7·2. $C_{20}H_{26}O_2N_4$ requires C, 67·8; H, 7·3%).

2-*Nitrotetramethylbenzidine*.—A mixture of tetramethylbenzidine (9·6 g.), sulphuric acid (140 c.c.), and nitric acid (2·8 c.c.), after being kept for 8 hours, was poured on to ice, and neutralised with ammonia. The dried product (m. p. 160°) crystallised from benzene as a dull red, crystalline powder, m. p. 164° (Found: C, 67·5; H, 6·8. $C_{16}H_{19}O_2N_3$ requires C, 67·4; H, 6·7%). The constitution of this compound follows from the fact that on further nitration it yields 2 : 2′-dinitrotetramethylbenzidine.

2 : (3′ ?)-*Dinitrotetramethylbenzidine*.—Sodium nitrite (2 g.) in

water (5 c.c.) was added to a solution of 2-nitrotetramethylbenzidine (2 g.) in cold acetic acid (60 c.c.). The precipitate thus formed crystallised from benzene–ligroin as a brilliant red powder, m. p. 145° (Found : C, 58·4; H, 5·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·4%).

(3 : 3′ ?)-*Dinitrotetramethylbenzidine.*—To tetramethylbenzidine (4·8 g.), dissolved in cold acetic acid (75 c.c.), was added a solution of sodium nitrite (4 g.) in water (10 c.c.). The solution assumed a deep green colour, but towards the end of the reaction this faded and the liquid filled with an orange precipitate, which crystallised from benzene in light red needles, m. p. 188°. The corresponding diamine, obtained by the same method as 2 : 2′-diaminotetramethylbenzidine, crystallised from alcohol in plates, m. p. 165—166° (mixed with 2 : 2′-diaminotetramethylbenzidine, it melted at 135°). With acetic anhydride, it gave a *diacetyl* derivative which separated from much alcohol as a white, crystalline powder, m. p. 281—282° (Found : C, 68·0; H, 7·3. $C_{20}H_{26}O_2N_4$ requires C, 67·8; H, 7·3%).

In an attempt to prepare tetranitrotetramethylbenzidine, 2 : 2′-dinitrotetramethylbenzidine (3·3 g.) was dissolved in sulphuric acid (40 c.c.), and nitric acid (1·5 c.c.) added. On being worked up in the usual way, the major part of the substance was recovered unchanged, but a small fraction, m. p. 185°, was obtained (Found : C, 50·8; H, 4·4%). This may be a trinitrotetramethylbenzidine ($C_{16}H_{17}O_6N_5$ requires C, 51·2; H, 4·5%).

Attempted Synthesis of the Dinitrotetramethylbenzidines.—The nitration of 4-iododimethylaniline (prepared by Baeyer's method, *Ber.*, 1905, **38**, 2762) proved unsuccessful, as either iodine was eliminated or blue products were formed (compare Merz and Weitz, *Ber.*, 1877, **10**, 746).

4-*Bromo*-3-*nitrodimethylaniline* was prepared (*a*) by the nitration of 4-bromodimethylaniline in the cold, (*b*) by the bromination of 3-nitrodimethylaniline (Ephraim and Hochuli, *Ber.*, 1915, **48**, 630). Although the yield obtained by method (*a*) was good, the product was accompanied by a trace of a substance which was removed with difficulty; this crystallised in short, crimson needles, m. p. 109—111°, from alcohol and was probably 4-bromo-3 : 5-dinitrodimethylaniline. Method (*b*) gave at once pure 4-bromo-3-nitrodimethylaniline, m. p. 95°. When this was heated with copper powder, an explosive reaction took place at about 170°. No reaction took place on prolonged boiling with copper powder in toluene—the absence of reaction might have been expected, since 4-bromo-3-nitrodimethylaniline was unchanged after heating under reflux with piperidine for 1½ hours.

4-*Benzylideneamino*-4′-*hydroxydiphenyl.*—4-Amino-4′-hydroxydiphenyl (5 g.) was warmed with benzaldehyde and alcohol (200 c.c.).

On cooling, the solution deposited plates, m. p. 200° (Found : N, 5·3. $C_{19}H_{15}ON$ requires N, 5·15%).

4-Acetylamino-4′-acetoxydiphenyl.—4-Amino-4′-hydroxydiphenyl was heated under reflux for 5 hours with a mixture of acetic anhydride and acetic acid. The product, recrystallised from acetic acid, formed plates, m. p. 218—220°. On prolonged keeping in pyridine solution with benzoyl chloride (1 mol.), it gave *4-acetylbenzoylamino-4′-acetoxydiphenyl*, which crystallised from alcohol in large, compact plates, m. p. 142—143° (Found : C, 73·9; H, 5·3. $C_{23}H_{19}O_4N$ requires C, 74·0; H, 5·1%). On hydrolysis with alcoholic sodium hydroxide this yielded 4-benzoylamino-4′-hydroxydiphenyl, which was also prepared by the addition of benzoyl chloride (1 mol.) to a solution of 4-amino-4′-hydroxydiphenyl in pyridine.

2-Aminodiphenyl was prepared by the method of Aeschlimann, Lees, McClelland, and Nicklin (J., 1925, **127**, 67). Owing to its feebly basic character, no suitable salts with optically active acids could be obtained.

Diphenyl-2-carboxylic acid, obtained by Pictet and Ankeromit's method (*Annalen*, 1891, **266**, 143), formed well-defined brucine and morphine salts, which were crystallised from several solvents, without, however, any indication of resolution being obtained. The strychnine and the quinine salts were obtained as viscous oils which could not be crystallised.

One of the authors (F. B.) wishes to acknowledge the receipt of a grant from the Advisory Council of the Department of Scientific and Industrial Research.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 13th*, 1926.]

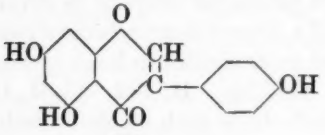
CCCLIX.—*Synthetical Experiments in the* iso*Flavone Group. Part II. A Synthesis of Methylgenistein (Methylprunetol) Dimethyl Ether and the Constitution of Prunetol (Genistein).*

By WILSON BAKER and ROBERT ROBINSON.

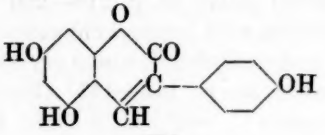
THE identity of genistein from *Genista tinctoria*, Linn. (Perkin and Newbury, J., 1899, **75**, 830; Horsfall and Perkin, J., 1900, **77**, 1312), with prunetol, obtained by demethylation of its monomethyl ether—prunetin (from *Prunus* bark;* Finnemore, *Pharm.*

* The botanical relations of the *Prunus* employed were not investigated by Finnemore, but Holmes (*Pharm. J.*, 1909, **28**, 191) states that it was intermediate between *P. avium* and *P. emarginata*.

J., 1910, **31**, 604)—was mooted as a possibility in Part I (J., 1925, **127**, 1981) and has now been proved by direct comparison (see p. 2716). Finnemore (*loc. cit.*) proposed the *iso*flavone constitution (I) for prunetol, whilst Bargellini * (*Gazzetta*, 1925, **55**, 949) has suggested its formulation as an α-pyrone (II).



(I.)



(II.)

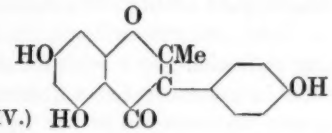
Although the behaviour of genistein and prunetol in most respects can be interpreted equally well by either formula, the nature of the products obtained on methylation of genistein and prunetin affords strong evidence of the correctness of Finnemore's supposition. Only two of the three hydroxyl groups of genistein and only one of the two in prunetin can be methylated by means of methyl iodide and alcoholic potassium hydroxide, whilst a by-product in the former case is a methylgenistein dimethyl ether still containing a free phenolic hydroxyl group. Such protection of a hydroxyl group from the action of the methylating agent, and also the methylation on carbon, recall the similar behaviour of members of the flavone series, *e.g.*, luteolin: the phenomena are inexplicable on the basis of formula (II). The synthetical experiments now recorded supply a conclusive proof that (I) represents genistein and prunetol and consequently that *iso*flavone derivatives occur in nature.

The methods which have been employed are based on those described in Part I and, in spite of numerous attempts to devise a more practicable synthesis of *iso*flavones bearing no substituent in position 2, we still find it necessary to proceed through the 2-styryl*iso*flavones and the *iso*flavonecarboxylic acids derived from these in small yield by oxidation.

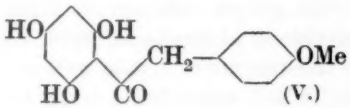
2 : 4 : 6-*Trihydroxyphenyl* p-*hydroxybenzyl ketone*, $C_6H_2(HO)_3 \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot OH$ (III), obtained from phloroglucinol and *p*-hydroxyphenylacetonitrile by an application of the Hoesch reaction, could be acetylated with formation of the acetyl derivative of 2-*methylgenistein* (IV) in poor yield, but could not be cinnamoylated with production of a chromone derivative. Much better results were obtained with the *methyl* ether (V) prepared from *p*-methoxyphenylacetonitrile

* In a letter dated September 27th, 1926, Professor Bargellini has informed us that he has synthesised the compound (II) and has found that its properties do not correspond with those of prunetol.

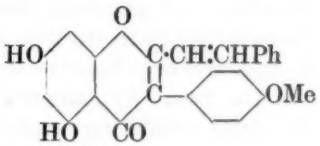
and phloroglucinol. Treatment of this ketone with a mixture of acetic anhydride and sodium acetate at 180°, followed by hydrolysis of the product, afforded 5 : 7-*dihydroxy*-4′-*methoxy*-2-*methyl*isoflavone (2-*methylgenistein* 4′-*methyl ether*) in satisfactory yield. 2-Methylgenistein, best obtained by demethylation of its 4′-methyl ether, closely resembles genistein (prunetol) in its properties. Cinnamoylation of (V) under closely-defined conditions yields the



(IV.)

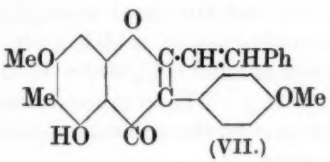


(V.)

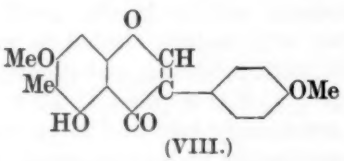


(VI.)

monocinnamoyl derivative (probably the 7-*cinnamate*) of 5 : 7-*dihydroxy*-4′-*methoxy*-2-*styryl*isoflavone (VI), which is itself obtained by the hydrolysis of the isolated primary product, again under conditions which do not allow of much variation. An excess of methyl iodide and sodium methoxide in boiling methyl-alcoholic solution converts (VI) into a C-*methyl* derivative of its 7-*methyl* ether (VII). We have assumed from analogies that the methyl



(VII.)



(VIII.)

group enters the position 6 in the phloroglucinol nucleus, but there is no clear proof that this is the case; the question of the situation of the methyl groups has, however, no bearing whatever on the validity of the argument here presented.

Attempts to oxidise the acetyl derivatives of (VI) and (VII) by potassium permanganate in pyridine solution gave benzoic acid only, but the oxidation of the acetyl derivative of (VII) by potassium permanganate in acetone solution gave benzoic and anisic acids along with an uncharacterised carboxylic acid which, after hydrolysis and decarboxylation by heating in glycerol, yielded the *iso*flavone (VIII). This was identical in all respects with methylgenistein dimethyl ether (Horsfall and Perkin, *loc. cit.*), with which it was directly compared.

EXPERIMENTAL.

Identity of Genistein and Prunetol.—We are greatly indebted to Professor A. G. Perkin for specimens of genistein and its dimethyl ether and to Mr. H. Finnemore for specimens of prunetol and prunetin and their derivatives. The genistein and prunetol differed but slightly in appearance; both specimens melted at 290—291° after softening and becoming red at about 284°. The behaviour of a mixture was the same. The specimens gave identical reactions: a pale yellow solution in alkalis; a violet coloration with ferric chloride in alcoholic solution, becoming brownish-green with excess of the reagent; a pale yellow solution in concentrated sulphuric acid which exhibited a weak bluish-green fluorescence in the light of an iron arc. The specimens of genistein dimethyl ether and prunetin methyl ether consisted of characteristic leaflets and could not be distinguished in appearance; both melted at 140—142°, as also did a mixture of the two. In sulphuric acid they gave identical pale yellow solutions exhibiting weak fluorescence and with alcoholic ferric chloride they developed the same reddish-purple coloration.

2 : 4 : 6-*Trihydroxyphenyl* p-*Hydroxybenzyl Ketone* (III).—A solution of *p*-hydroxyphenylacetonitrile (10 g.) and anhydrous phloroglucinol (9·4 g.) in dry ether (75 c.c.) was saturated with hydrogen chloride at 0° and again after 24 hours. The crystalline crust of *ketimine hydrochloride* was washed with ether and heated with water for 1 hour; the ketone (12 g.) then separated. It is very sparingly soluble in the usual organic solvents and crystallises from 50% methyl alcohol in microscopic needles which melt at 259° with reddening and decomposition (Found: C, 60·4; H, 5·0. $C_{14}H_{12}O_5,H_2O$ requires C, 60·4; H, 5·1%). The combined water is tenaciously held and in general properties the substance closely resembles its higher homologue, phloretin.

5 : 7 : 4′-*Trihydroxy*-2-*methyl*isoflavone (2-*methylgenistein*) (IV) is most readily prepared by demethylation of its 4′-methyl ether (see below) by means of boiling hydriodic acid (*d* 1·7). It was first obtained in the following manner. A mixture of the above-described tetrahydroxydeoxybenzoin (5 g.), sodium acetate (5 g.), and acetic anhydride (25 c.c.) was heated at 190—200° for 48 hours; the dark product then obtained by decomposition and washing with water was dissolved in a very small amount of acetic acid. Crystals separated slowly and after a long time these were freed from adhering oil by contact with porous porcelain and thrice crystallised from acetic acid (charcoal). The thin, pinkish prisms, m. p. 171° (Found: C, 65·3; H, 4·7. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%), were insoluble in cold, aqueous sodium hydroxide, but gave a violet

coloration with alcoholic ferric chloride. The substance is doubtless 5-*hydroxy*-7 : 4′-*diacetoxy*-2-*methyl*isoflavone, since several substituted 5-hydroxybenzochromones are already known which are insoluble in aqueous alkalis and yet give a positive ferric chloride reaction. The parent substance, obtained by hydrolysis with aqueous sodium carbonate, crystallised from very dilute alcohol in colourless needles containing $1H_2O$, m. p. 258—259° (slight decomp.) (Found in anhydrous substance: C, 67·2; H, 4·4. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·3%). Ferric chloride added to an alcoholic solution gives a violet and then a brownish-green coloration. Solutions in aqueous sodium hydroxide and in concentrated sulphuric acid are pale yellow and the latter exhibits a weak bluish-green fluorescence. In all these properties and in its solubility relations this compound exhibits a noteworthy resemblance to genistein. The O-*triacetyl* derivative was readily obtained in the usual manner (therefore the formation of a diacetyl derivative which is noted above is almost certainly due to hydrolysis in the isolation process rather than to incomplete acetylation) and crystallised from alcohol, in which it was sparingly soluble, in colourless, silky needles, m. p. 214° (Found: C, 64·4; H, 4·5. $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4%).

2 : 4 : 6-*Trihydroxyphenyl* p-*Methoxybenzyl Ketone* (V).—*p*-Methoxyphenylacetonitrile (20 g.) (obtained in excellent yield by methylation of *p*-hydroxyphenylacetonitrile with methyl sulphate and aqueous potassium hydroxide at about 50°) and phloroglucinol (20 g.), when treated as in the similar case described above, gave 30 g. of the almost pure ketone. This crystallises from 50% methyl alcohol in minute, colourless prisms, m. p. 192—193° (Found: C, 62·0; H, 5·7. $C_{15}H_{14}O_5,H_2O$ requires C, 61·7; H, 5·5%). The substance is only slowly dehydrated at 140°; ferric chloride added to an alcoholic solution develops a reddish-purple coloration; and the solutions in alkalis are yellow.

5 : 7-*Dihydroxy*-4′-*methoxy*-2-*methyl*isoflavone (4′-*Methyl Ether of IV*).—The acetylation of the foregoing ketone was carried out in the usual way, the mixture being heated at 180° for 20 hours. A *diacetyl* derivative was obtained in almost quantitative yield after treatment of the reaction product with water; this crystallised from ethyl alcohol in colourless needles, m. p. 208—209° (Found: C, 65·7; H, 4·9. $C_{21}H_{18}O_7$ requires C, 66·0; H, 4·7%). The parent substance, obtained by hydrolysis, crystallises from not too much alcohol in prisms, m. p. 205° (Found: C, 68·2; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). This *iso*flavone gives colourless solutions in aqueous alkalis and the addition of ferric chloride to an alcoholic solution produces a reddish-violet and

then a brownish-green coloration. The colourless solution in concentrated sulphuric acid exhibits a very weak bluish-green fluorescence. On methylation with methyl sulphate and aqueous potassium hydroxide, a mixture of the mono- and di-methyl ethers is produced; these separate together from alcohol, the former in feathery crystals and the latter in quadrilateral plates. The two forms were sorted out and separately crystallised from alcohol. *5-Hydroxy-7 : 4′-dimethoxy-2-methylisoflavone* crystallises in colourless needles, m. p. 197—199° (Found: C, 69·6; H, 5·5. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). It was also obtained by the use of methyl iodide. The reactions of the substance closely resemble those of genistein dimethyl ether.

5 : 7 : 4′-Trimethoxy-2-methylisoflavone, m. p. 175—176° (Found: C, 70·0; H, 5·8. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%), does not give a ferric chloride reaction in alcoholic solution. Its pale yellow solution in concentrated sulphuric acid exhibits a blue fluorescence.

5 : 7-Dihydroxy-4′-methoxy-2-styrylisoflavone (VI).—An efficiently stirred mixture of anhydrous 2 : 4 : 6-trihydroxyphenyl *p*-methoxybenzyl ketone (10 g.) and cinnamic anhydride (100 g.) was heated (oil-bath at 180—200°) for 2 hours; powdered sodium cinnamate (10 g.) was then slowly introduced and the heating continued for 6 hours. The pasty product was scraped out while hot, ground under water, washed with much water and with aqueous sodium carbonate, and dried at a moderate temperature. The chocolate-coloured powder was added to alcohol (250 c.c.) and concentrated sulphuric acid (5 c.c.), and decomposition of the excess of cinnamic anhydride effected by gentle warming for 1½ hours followed by boiling for 1 hour. After cooling, the solid was collected and washed with alcohol. It crystallised from 1 litre of glacial acetic acid (charcoal) in thin, bright yellow, microscopic prisms, m. p. 230—231° (yield 8 g.) (Found: C, 76·6; H, 4·9. $C_{33}H_{24}O_6$ requires C, 76·7; H, 4·7%). This substance appears to be *5-hydroxy-7-cinnamoyloxy-4′-methoxy-2-styrylisoflavone* (hydrolysis yielded 83·5% of the theoretical amount of cinnamic acid), the situation of the cinnamoyl group being inferred from the insolubility of the compound in aqueous sodium hydroxide, even on boiling, and from the green coloration developed in alcoholic solution with ferric chloride. (This reaction is weak on account of the extremely sparing solubility of the substance in alcohol.) The cinnamate (10 g.) was treated with a boiling mixture of alcohol (200 c.c.), potassium hydroxide (4 g.), and water (10 c.c.) for ¾ hour, after which water (200 c.c.) was introduced and the liquid saturated with carbon dioxide. The bright yellow precipitate was isolated; the substance crystallised from a large volume of alcohol in yellow

needles, m. p. 278—279°, containing 1EtOH (yield about 7 g.) (Found in material dried at 100°: C, 74·9; H, 5·0. $C_{24}H_{18}O_5$ requires C, 74·6; H, 4·7%). An alcoholic solution becomes reddish-brown on the addition of ferric chloride. The solubility of the substance in cold aqueous sodium hydroxide is slight, but on heating, a viscous, orange solution is produced; this froths readily and on cooling deposits colloidal flocks that become crystalline on the addition of alcohol. The *diacetyl* derivative, obtained in the usual manner, crystallises from acetic acid in yellow, microscopic needles, m. p. 225—226° (Found: C, 69·3, 69·3; H, 5·0 5·0; $C_2H_4O_2$, by direct loss on fusion, 6·5. $C_{28}H_{22}O_7,0·5C_2H_4O_2$ requires C, 69·6; H, 4·8; $C_2H_4O_2$, 6·0%). Several attempts to oxidise this diacetate so as to produce a substituted *iso*flavone-carboxylic acid were fruitless.

5-Acetoxy-7 : 4′-dimethoxy-2-styryl-6-methylisoflavone (*Acetyl* derivative of VII).—A mixture of dihydroxymethoxystyryl*iso*flavone (8 g.), methyl alcohol (200 c.c.), sodium methoxide (from 2·3 g. of sodium), and an excess of methyl iodide was refluxed for 48 hours (more sodium methoxide and methyl iodide were added after 24 hours). The product, after being heated with dilute aqueous sodium hydroxide, in which it was insoluble, crystallised from much alcohol in thin, bright yellow prisms, m. p. 217—218°. *5-Hydroxy-7 : 4′-dimethoxy-2-styryl-6-methylisoflavone* (VII) gives a green coloration with ferric chloride, and with acetic anhydride yields the *acetyl* derivative, which crystallises from ethyl alcohol in very fine, pale yellow needles, m. p. 218—219° (Found: C, 73·7; H, 5·5. $C_{28}H_{24}O_6$ requires C, 73·7; H, 5·3%). All the above styryl derivatives give bright yellow solutions in sulphuric acid and these exhibit a weak, green fluorescence.

Methylgenistein (*Methylprunetol*) *Dimethyl Ether* (VIII).—(A) Crabtree and Robinson (J., 1918, **113**, 868) indicated that *C*-methylation of resacetophenone by methyl iodide precedes *O*-methylation and is favoured by an increase in the concentration of alkali-metal alkyloxide in the solution. Accordingly we methylated prunetol by refluxing it for 12 hours with a methyl-alcoholic solution of sodium methoxide (10 mols.) and an excess of methyl iodide; the only isolable product was methylprunetol (methylgenistein) dimethyl ether (compare Perkin and Horsfall, *loc. cit.*) which, after two crystallisations from alcohol, formed tiny, colourless needles or prismatic needles, m. p. 200—201·5° (Found: C, 69·3; H, 5·4. Calc. for $C_{18}H_{16}O_5$: C, 69·2; H, 5·2%).

(B) Finely-powdered potassium permanganate (5·6 g., a 20% excess) was gradually added during 4 hours to a solution of acetoxydimethoxymethylstyryl*iso*flavone (5 g.) in pure acetone (600

c.c.) cooled at −10° to −15°, which was continuously stirred and through which a stream of carbon dioxide was led. Towards the end of the operation a slight rise of temperature was permitted. Water was added and, after removal of acetone and a trace of benzaldehyde in a current of steam, the filtered liquid was concentrated to a small volume, saturated with carbon dioxide and filtered. On acidification, a mixture of tarry material and some white crystals was precipitated and from this a small quantity of benzoic acid was sublimed. The crystalline constituent, of which a further quantity was obtained by extraction of the tar with boiling water, proved to be anisic acid. The residue was dissolved in aqueous sodium bicarbonate and the solution boiled, filtered, and acidified. The brown, crystalline precipitate was collected, dried at 100° (to a viscous mass), and heated with anhydrous glycerol at 250° for ½ hour. The product was mixed with water and sodium bicarbonate and extracted with ether. The brown residue, after removal of the solvent from the combined extracts, crystallised very readily from alcohol in minute, colourless needles, m. p. 198—200·5° (after three crystallisations; yield, 0·05 g.) (Found: C, 69·0; H, 5·3%).

A mixture of the products obtained in (A) and (B) had m. p. 199—201° and the melt crystallised at once on cooling. The specimens were indistinguishable in appearance, in crystalline form, and in their solubility relations and reactions. The pale yellow solution in sulphuric acid was devoid of fluorescence and the addition of ferric chloride to an alcoholic solution developed a violet coloration, which became olive-green with an excess of the reagent.

We desire to thank the Royal Society and the Chemical Society for grants which have defrayed a large portion of the expenses of the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, August 13th*, 1926.]

CCCLX.—*The Condensation of Phenols with Chloral.*

By FREDERICK DANIEL CHATTAWAY.

CHLORAL reacts with phenols in presence of sulphuric acid, yielding more complicated compounds than any hitherto described.

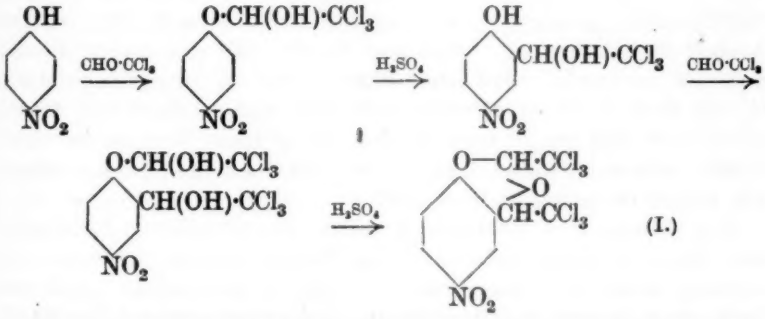
For example, when *p*-nitrophenol and chloral are brought together

in presence of a large excess of concentrated sulphuric acid, a beautifully crystalline solid is formed whose composition and molecular weight are expressed by the formula $C_{10}H_5O_4NCl_6(OH{\cdot}C_6H_4{\cdot}NO_2 + 2CCl_3{\cdot}CHO - H_2O)$.

No phenolic or alcoholic hydroxyl group is present in the molecule, since the compound does not dissolve in dilute alkalis and can be recrystallised without change from boiling acetic anhydride. It contains the nitro-group unchanged, since this can be reduced to an amino-group which can be acetylated, or diazotised and replaced or removed.

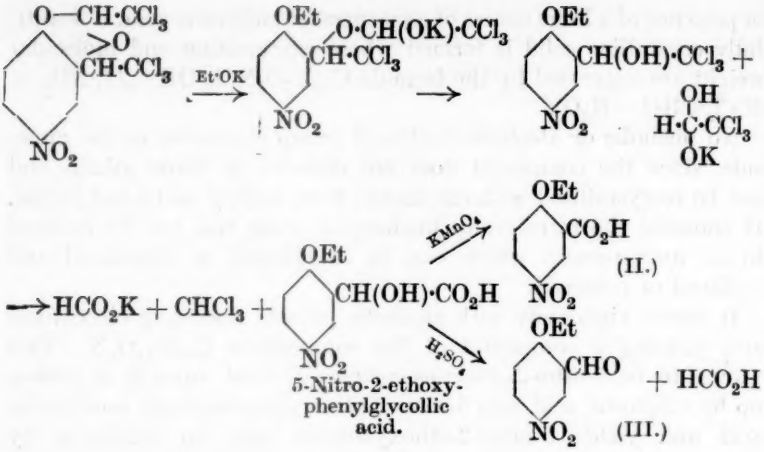
It reacts vigorously with alcoholic potash, liberating chloroform and yielding a compound of the composition $C_{10}H_{11}O_6N$. This proves to be *5-nitro-2-ethoxyphenylglycollic acid*, since it is broken up by sulphuric acid into 5-nitro-2-ethoxybenzaldehyde and formic acid and yields 5-nitro-2-ethoxybenzoic acid on oxidation by aqueous alkaline permanganate.

The condensation therefore appears to take the following course. The *p*-nitrophenol and chloral first unite to form a compound resembling chloral alcoholate in structure, which then, under the influence of the sulphuric acid, undergoes intramolecular rearrangement, the migrating $-CH(OH){\cdot}CCl_3$ group taking up the ortho-position in the nucleus, the para-position being already occupied by the nitro-group. A further similar combination followed by elimination of water yields the final product, which is therefore *anhydro-5-nitro-2-ββββ-trichloro-α-hydroxyethoxy-1-ββββ-trichloro-α-hydroxyethylbenzene* (I).



(I.)

The reaction of this compound (I) with alcoholic potash and the subsequent oxidation of the product to 5-nitro-2-ethoxybenzoic acid (II) and its conversion by sulphuric acid into 5-nitro-2-ethoxybenzaldehyde (III) and formic acid may be represented as follows :



EXPERIMENTAL.

Anhydro-5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I).—Chloral hydrate (331 g.; 2 mols.) and 139 g. of *p*-nitrophenol (1 mol.) were heated together in an open dish until a clear brown liquid was formed. When this was poured, with constant stirring, into 1000 c.c. of concentrated sulphuric acid, no evolution of heat occurred and the colour of the mixture, the temperature of which did not rise above 35°, gradually deepened until it became dark greenish-brown. The mixture, which was frequently shaken to prevent the formation of a compact crust, after 5—8 days had become a pulp of colourless crystals of the condensation product. This was filtered off and thoroughly washed first with warm water and finally with warm very dilute aqueous ammonia until the filtrate was no longer yellow; it was then dried on a water-bath, and recrystallised first from acetic acid and finally from alcohol, being thus obtained in very faintly yellow crystals. Usually the yield is somewhat less than the weight of chloral hydrate used.

The substance is insoluble in water, dilute acids and alkalis, but dissolves moderately easily in boiling alcohol, benzene, or acetone, easily in boiling acetic acid, giving pale yellow solutions from which it separates in glistening, colourless prisms, m. p. 146° (Found: C, 28·9; H, 1·3; N, 3·5; Cl, 51·1; *M*, ebullioscopic in benzene and acetone, 418, 423. $C_{10}H_5O_4NCl_6$ requires C, 28·9; H, 1·2; N, 3·4; Cl, 51·2%; *M*, 416). The compound was recovered unchanged after being heated for several hours on a water-bath with a large excess of acetic anhydride. 100 G. of alcohol dissolve 2·51 g. at 15·6°, 2·78 g. at 21°, and 3·78 g. at 30°.

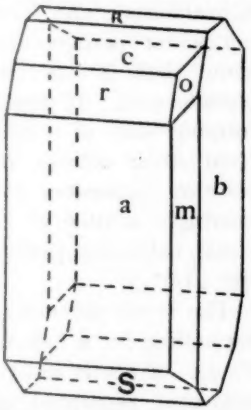
Mr. Curjel of Keble College, who has very kindly examined the crystals, describes them as follows:

Well-formed, colourless crystals were obtained by allowing a solution in alcohol to cool slowly. The crystals belong to the holohedral class of the anorthic system. The axial elements are $a:b:c = 2{\cdot}4895:1:1{\cdot}1368$; $\alpha = 90°\ 28'$, $\beta = 115°\ 32'$, $\gamma = 81°\ 8'$. The forms observed were a {100}, m {110}, b {010}, r {101}, c {001}, R {$\bar{1}$01}, S {20$\bar{1}$}, and o {111}.

The interfacial angles are given in the accompanying table.

Angle.	No. of measurements.	Limits.	Mean observed.	Calc.
100 : 110	10	74° 42′—75° 13′	75° 0′	—
110 : 010	10	24° 29′—24° 45′	24° 36′	—
100 : 101	6	44° 54′—45° 15′	45° 6′	—
010 : $\bar{1}$01	4	89° 10′—89° 17′	89° 14′	—
100 : $\bar{1}$01	6	91° 37′—91° 55′	91° 48′	—
101 : 001	6	18° 53′—19° 7′	19° 1′	19° 8′
$\bar{1}$01 : $\bar{2}$01	4	26° 29′—26° 43′	26° 38′	26° 50′
110 : 111	4	38° 12′—38° 21′	38° 16′	38° 24′
111 : 001	4	43° 35′—45° 1′	44° 28′	44° 44′
0$\bar{1}$0 : 101	4	83° 33′—83° 42′	83° 36′	83° 34′
010 : 001	2	93° 32′—93° 36′	93° 34′	93° 42′
101 : 111	2	43° 25′—43° 29′	43° 27′	43° 46′

The predominant forms are a {100} and b {010}. There are fair cleavages parallel respectively to a {100} and b {010}. A cleavage fragment parallel to either of these faces shows one optic axis, when examined in convergent light between crossed Nicols. The crystals are biaxial, with a fairly wide axial angle. The double refraction is negative and very strong. The interference figure exhibits crossed dispersion. $\rho > v$.



The specific gravity of the crystals was found by the suspension method to be 1·733 at 19°, a Westphal balance being used.

Conversion of Anhydro-5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene into dl-5-*Nitro-2-ethoxyphenylglycollic Acid*, $NO_2{\cdot}C_6H_3(OEt){\cdot}CH(OH){\cdot}CO_2H$.—The anhydro-compound (50 g.; 1 mol.) was gradually added to a solution of 60 g. of potassium hydroxide (about 9 mols.) in 200 c.c. of alcohol, the vigorous action which took place being moderated by cooling. Chloroform was liberated and ethyl orthoformate produced, both of which could be recognised by their smell. The deep brownish-yellow liquid produced (a little of which gave a clear, deep yellow solution on being heated with an excess of water) was partly neutral-

ised by addition of hydrochloric acid, until distinctly but not very strongly alkaline, the alcohol was then distilled off in steam, and the resulting clear yellow liquid made strongly acid with hydrochloric acid. A small quantity of a pale brownish-yellow solid separated, which was decolorised by animal charcoal and recrystallised several times from boiling water, in which it was sparingly soluble; *5-nitro-2-ethoxybenzoic acid* was thus obtained in thin, colourless plates, m. p. 163° (Found : C, 51·2; H, 4·4; N, 6·75. $C_9H_9O_5N$ requires C, 51·1; H, 4·3; N, 6·6%). The yield was less than 1% of the weight of the condensation product decomposed.

The strongly acid mother-liquor from which the 5-nitro-2-ethoxybenzoic acid had been filtered, on standing for about 24 hours, deposited a large quantity of another acid in very pale brownish-yellow crusts. This acid was moderately easily soluble in boiling water and very easily soluble in boiling alcohol, giving clear yellow solutions. From an alcoholic solution to which boiling water (10—12 vols.) had been added, it separated, on cooling, in aggregates of small, almost colourless plates or flattened prisms showing a faint yellow tint, m. p. 138° (Found : C, 49·7; H, 4·6; N, 5·9. $C_{10}H_{11}O_6N$ requires C, 49·8; H, 4·6; N, 5·8%). Its composition and the facts that it contains an ethoxyl, a hydroxyl, and a carboxyl group, that it is decomposed by sulphuric acid into 5-nitro-2-ethoxybenzaldehyde and formic acid, and that on oxidation by alkaline potassium permanganate it yields 5-nitro-2-ethoxybenzoic acid, show that it has the constitution of dl-*5-nitro-2-ethoxyphenylglycollic acid*. It dissolves in alkalis and in a solution of ammonia, forming salts of a deep yellow colour. The *silver* salt, prepared from silver nitrate and the ammonium salt in strong neutral solution, separates as a thick, white, crystalline pulp, which is sparingly soluble in boiling water and crystallises on cooling in small, colourless plates (Found : Ag, 30·6. $C_{10}H_{10}O_6NAg$ requires Ag, 31·0%).

The *acetyl* derivative, $NO_2{\cdot}C_6H_3(OEt){\cdot}CH(OAc){\cdot}CO_2H$, prepared by boiling for a few minutes a solution of the acid (5 g.) in about 10 c.c. of acetic anhydride containing two drops of strong sulphuric acid, separated, on cooling after the addition of a few drops of water, as a white, crystalline solid. It was easily soluble in boiling chloroform and sparingly soluble in light petroleum, and separated from a mixture of the two in very small, rhombic plates, m. p. 147·2° (Found : C, 50·9; H, 4·75; N, 5·0. $C_{12}H_{13}O_7N$ requires C, 50·9; H, 4·6; N, 4·95%).

Decomposition of dl-*5-Nitro-2-ethoxyphenylglycollic Acid into 5-Nitro-2-ethoxybenzaldehyde and Formic Acid by Concentrated Sulphuric Acid.*—The *dl*-acid (5 g.) was gently heated with about 6 c.c.

of concentrated sulphuric acid, carbon monoxide being evolved at 60—70° and a deep yellow solution obtained. This was cooled and poured into water; 5-nitro-2-ethoxybenzaldehyde then separated as a pale yellow solid. This was dissolved in acetic acid and warmed with semicarbazide hydrochloride and excess of sodium acetate.

5-Nitro-2-ethoxybenzaldehydesemicarbazone,

$$NO_2 \cdot C_6H_3(OEt) \cdot CH{:}N \cdot NH \cdot CO \cdot NH_2,$$

thus obtained as a yellowish-white solid, exists in two very well-characterised, polymorphic forms. It is somewhat sparingly soluble in boiling alcohol and, on cooling, the labile form separates in slender, flattened prisms, so thin that they curl up like watch springs. On standing, the stable form soon makes its appearance as small, compact, golden-yellow, rhombic prisms or plates; these grow at the expense of the labile form, which dissolves and in a few days completely disappears. Both forms melt at 234—235° with decomposition and evolution of gas (Found: C, 47·9; H, 5·2; N, 22·1. $C_{10}H_{12}O_4N_4$ requires C, 47·6; H, 4·8; N, 22·2%).

Oxidation of dl-*5-Nitro-2-ethoxyphenylglycollic Acid.*—The *dl*-acid (10 g.) was dissolved in the smallest possible quantity of a strong aqueous solution of potassium hydroxide, a solution of 6 g. of potassium permanganate in about a litre of hot water added, and the whole boiled vigorously for about ½ hour. The excess of permanganate was destroyed with alcohol, the manganese dioxide filtered off, and to the bright yellow filtrate a slight excess of hydrochloric acid was added. The colourless solution obtained, on cooling, deposited *5-nitro-2-ethoxybenzoic acid*, which crystallised from boiling water, in which it was somewhat sparingly soluble, in almost colourless, long, irregularly grown, thin, rhombic plates with a faint yellow tint, m. p. 163° (Found: C, 51·0; H, 4·3; N, 6·7. $C_9H_9O_5N$ requires C, 51·1; H, 4·3; N, 6·6%). It dissolves in aqueous potassium hydroxide, giving an intense deep yellow solution, and forms a very sparingly soluble *sodium* salt which crystallises from aqueous solution in small, bright yellow prisms.

The acid was identical with a specimen of 5-nitro-2-ethoxybenzoic acid made by nitrating salicylic acid, converting the 5-nitrosalicylic acid into ethyl 5-nitro-2-ethoxybenzoate, saponifying this by caustic potash, and acidifying the product.

*Anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-*1-*βββ-trichloro-α-hydroxyethylbenzene* (formula similar to I).—The corresponding 5-nitro-compound (10 g.) was dissolved in 30 c.c. of acetic acid, and about 20 g. of granulated tin were added; the heat of reaction

caused the liquid to boil freely. When vigorous action had ceased, the liquid was allowed to cool and then poured into concentrated hydrochloric acid (4—5 vols.). The *hydrochloride* of the base, which separated in an almost pure condition as a colourless solid, crystallised from boiling dilute hydrochloric acid, in which it was moderately easily soluble, in thin, colourless plates which when heated decomposed without melting. It was easily soluble in alcohol (Found: Cl, 58·6. $C_{10}H_7O_2NCl_6$,HCl requires Cl, 58·7%). On warming the hydrochloride with a dilute solution of sodium carbonate, the *base* was liberated as a white solid. It crystallised from boiling alcohol, in which it was readily soluble, in long, colourless, flattened, very slender, hair-like prisms, m. p. 176° (Found: N, 3·7. $C_{10}H_7O_2NCl_6$ requires N, 3·6%).

The *acetyl* derivative was formed with evolution of heat when the base was added to acetic anhydride. It is readily soluble in alcohol, dilute acetic acid, and chloroform and sparingly soluble in light petroleum. It separates from a mixture of the last two solvents in thin, colourless, rhombic plates, m. p. 206° (Found: C, 33·7; H, 2·1; N, 3·3; Cl, 49·8. $C_{12}H_9O_3NCl_6$ requires C, 33·5; H, 2·1; N, 3·4; Cl, 49·6%).

The *5-diazonium chloride* was readily formed when nitrous fumes were passed into a solution, at 0°, of 15 g. of the preceding hydrochloride in about 50 c.c. of alcohol through which a little dry hydrogen chloride had been passed.

The *sodium* salt of the 5-azo-β-naphthol derivative separated as a brilliant scarlet precipitate when a solution of the preceding diazonium salt was poured into a cooled solution of β-naphthol in excess of aqueous caustic soda. After the liquids had been made slightly acid with acetic acid, the scarlet *azo*-compound was filtered off. It crystallised from boiling acetic acid, in which it was readily soluble, in long, deep red needles, m. p. 196° (Found: Cl, 39·3. $C_{20}H_{12}O_3N_2Cl_6$ requires Cl, 39·4%).

Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene, $C_6H_4\begin{cases}O\cdot CH\cdot CCl_3\\ >O\\ CH\cdot CCl_3\end{cases}$.—A solution of the diazonium chloride in alcohol obtained as described above from 15 g. of the amine hydrochloride was heated and finally boiled gently for some minutes. The liquid became dark coloured, nitrogen was steadily evolved, and aldehyde was liberated. The whole was then poured into water, when *anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene* separated as a slightly brown solid. It crystallised from boiling alcohol, in which it was moderately easily soluble, in clusters of colourless, very thin, slender, flattened

prisms, m. p. 119° (Found : C, 32·5; H, 1·7; Cl, 37·5. $C_{10}H_6O_2Cl_6$ requires C, 32·4; H, 1·6; Cl, 37·35%).

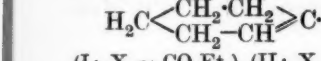
The action of chloral upon other phenols and phenolic compounds in presence of concentrated sulphuric acid is being studied.

THE QUEEN'S COLLEGE, OXFORD. [*Received, March 31st,* 1926.]

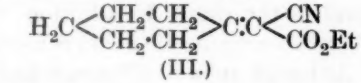
CCCLXI.—*The Chemistry of the Three-carbon System. Part VII. Derivatives of Malonic Acid.*

By GEORGE ARMAND ROBERT KON and ERIC ALFRED SPEIGHT.

THE distinction between the mobility and the point of equilibrium of a tautomeric system has been emphasised by Kon and Linstead (J., 1925, **127**, 616). The mobility of the system appears to be principally connected with the efficiency of the activating group, usually known as the "enolising efficiency" when the term is applied to systems exhibiting keto-enol tautomerism; it must depend ultimately on the capacity of this group to cause the potentially mobile hydrogen atom to move towards one of the atoms constituting it, this movement being accompanied by a rearrangement of the multiple linkings which the group contains. For example, the carbethoxyl group, which has a low enolising efficiency according to Claisen's rule (compare Dieckmann, *Ber.*, 1922, **55**, 2470), has but little effect in promoting the mobility of a three-carbon system, whereas the more active acetyl group has a much greater effect; the difference is well exemplified by a comparison of the ester (I) with *cyclo*hexenylacetone (II).



(I; X = CO_2Et.) (II; X = COMe.)



(III.)

The position of equilibrium, which is, of course, a measure of the relative stabilities of the two forms ($\alpha\beta$ * and $\beta\gamma$ in a three-carbon system), is the resultant of several effects. One of these is again due to the activating group, in virtue of the tendency of a double bond to become conjugated with the double or triple bond of the activating group. Another effect, which may operate in the same or in the opposite sense, can be due to the presence of a second unsaturated group (another activating group or phenyl) or to a structural condition capable of stabilising the double bond in a given position; an example of the latter type is the influence of the *cyclo*pentane or *cyclo*hexane ring or of a suitable *gem*-group in the β-position of a three-carbon system. It follows that the

* The carbon atom to which the activating group is attached is called α in all cases.

attachment of a second activating group to the α-carbon atom, reinforcing the first one, not only enhances the mobility of the system, but also tends to stabilise the αβ-phase of the compound, since the double bond in this position is doubly conjugated; these effects are apparent in ethyl α-cyano*cyclo*hexylideneacetate (III), which, unlike the compounds (I) and (II), normally occurs in the αβ-form.

In accordance with Claisen's rule, the introduction of a second carbethoxyl group into the ester (I) in the α-position should produce, both on the mobility of the system and on the point of equilibrium, effects similar to, but less pronounced than, those of the cyano-group. This view receives support from a study of several esters prepared by condensing ethyl malonate with appropriate ketones; the first member of the series, ethyl *iso*propylidenemalonate (IV), has already been prepared by Meyenberg (*Ber.*, 1895, **28**, 785).

(IV.) $CMe_2{:}C(CO_2Et)_2$ $\qquad$ $CH_2{\cdot}CH_2{>}C{:}C(CO_2Et)_2$ (V.)
$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2{\cdot}CH_2$

$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CH\end{matrix}{>}C{\cdot}CH(CO_2Et)_2 \quad \text{(VI.)}$$

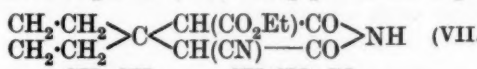
The most striking feature of this series is the point of equilibrium in the compounds (V) and (VI). The ester (V), like ethyl *iso*-propylidenemalonate, has the αβ-unsaturated structure; it gives *cyclo*pentanone on oxidation and shows an exaltation of the molecular refraction. The *cyclo*hexane compound, on the other hand, has the βγ-unsaturated formula (VI) as shown by its optical properties; on oxidation with ozone it gives Δ^1-*cyclo*pentenyl methyl ketone, which can only be derived from a compound with a double bond in the ring. In addition, the acid corresponding to it gives Δ^1-*cyclo*hexenylacetic acid on heating.

Although such a difference had not previously been observed, it was clearly to be expected, since the *cyclo*hexane ring has a much greater tendency to acquire a double bond than the *cyclo*pentane ring (compare Dieckmann, *loc. cit.*) and therefore is capable of overcoming the attraction of the two carboxyl groups.

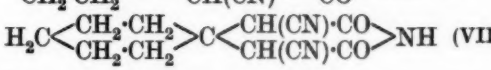
This observation is of considerable interest; there is little doubt that a relationship exists between the internal strain in a ring consequent upon the alteration of the normal tetrahedral angle and the tendency of the ring to acquire a double bond. A similar effect probably accounts for the tendency of the double bond to move towards the βγ-position in ββ-diethylacrylic acid (Kon and Linstead, *loc. cit.*). A more detailed discussion of this relationship is reserved for a future communication.

The mobility of the hydrogen atom in this series is somewhat difficult to gauge owing to certain peculiarities of the compounds.

For example, it is very difficult to demonstrate the existence of the αβ-phase by the usual addition reactions. Even the ester (V), which has unquestionably the αβ-structure, does not readily undergo the Michael reaction in presence of sodium, no doubt on account of the great tendency to form its own sodio-derivative; * we have, however, succeeded in obtaining an addition product with hydrogen cyanide and in condensing the ester (V) with ethyl cyanoacetate and ammonia, the compound (VII) being produced in poor yield.



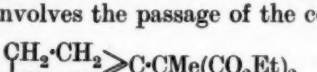
(VII.)



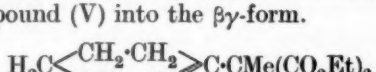
(VIII.)

The ester (VI) did not yield a similar compound, the product being the well-known imide (VIII), the formation of which is best explained by assuming that the condensation product first formed undergoes fission, ethyl malonate being eliminated (compare Scheiber and Meisel, *Ber.*, 1915, **48**, 238) and a further molecule of ethyl cyanoacetate being then added on. This reaction was not observed if the ester had been prepared by the action of ethyl iodide on the silver salt of the pure solid acid, although both the ester prepared by direct condensation and that obtained by esterification of the acid by Fischer's method gave the same poor yield of the imide. The pure ester reacts with ethyl sodiocyanoacetate to a limited extent; the condensation product, however, again appears to undergo fission, eliminating ethyl malonate, for a nitrogenous fraction is isolated which readily condenses with ethyl cyanoacetate and ammonia to give the imide (VIII) and therefore probably consists of ethyl α-cyano*cyclo*hexylideneacetate (III). It would thus appear that the pure ester is non-mobile under the conditions of the Guareschi reaction and requires the presence of a powerful reagent to "equilibrate" it; we were, however, unable to effect such an equilibration even by the prolonged action of hot sodium ethoxide, perhaps for the reason above.

Both esters (V and VI) very readily yield sodio-derivatives by the action of sodium in methyl- or ethyl-alcoholic solution. By the action of methyl iodide on these the corresponding α-methyl derivatives (IX and X) were produced in good yield; the reaction involves the passage of the compound (V) into the βγ-form.



(IX.)



(X.)

* It is presumably for a similar reason that ethyl acetonedicarboxylate cannot be condensed with ethyl cyanoacetate either by Michael's or by Gaureschi's method (unpublished observation).

Ethyl *iso*propylidenemalonate also can be alkylated with comparative ease, giving the *ester*, $CH_2{:}CMe{\cdot}CMe(CO_2Et)_2$: the production of a terminal methylene group by the movement of a hydrogen atom away from a *gem*-dimethyl group usually occurs with some difficulty. The *acid* corresponding to this ester loses carbon dioxide on heating and passes into a liquid *acid* which must have the formula $CH_2{:}CMe{\cdot}CHMe{\cdot}CO_2H$; this is not identical with trimethylacrylic acid (Perkin, J., 1896, **69**, 1480) but passes into it on boiling with strong alkalis. It is proposed to investigate this change at a later date.

Experimental.

Methylation of Ethyl iso*Propylidenemalonate* (IV).—To a solution of 2·3 g. of sodium in 30 c.c. of ethyl alcohol was added the ester (Meyenberg, *loc. cit.*) (0·1 g.-mol.), followed slowly by an excess of methyl iodide. The deep orange colour of the liquid faded and the reaction was complete after 2 hours' warming. Water and dilute hydrochloric acid were added and the oil was taken up in ether and washed with sodium carbonate, which removed some acid material. The extract was washed, dried, and evaporated, and after two methylations an *ester* was obtained, b. p. 124°/18 mm., $d_4^{24°}$ 1·01159, $n_D^{24°}$ 1·44020, $[R_L]_D$ 55·81 (calc., 55·84). We have not yet succeeded in oxidising this ester.

The methylated ester was hydrolysed by 64% aqueous potassium hydroxide and a little alcohol in ½ hour. The *acid*, isolated by means of ether, readily solidified. It contained a little of the parent acid (m. p. 170—171°) which, being almost insoluble in chloroform, was removed by extracting the mixture with this solvent. Addition of petroleum to the solution gave a substance from which, after several crystallisations from chloroform–petroleum and finally from hydrochloric acid, the new acid was obtained in flattened needles, m. p. 135° (decomp.) (Found : C, 53·3; H, 6·3. $C_7H_{10}O_4$ requires C, 53·2; H, 6·2%).

The acid was heated under reduced pressure until no more carbon dioxide was evolved. The residue, on distillation, gave a colourless, mobile oil, b. p. 108°/25 mm., having the characteristic odour of the acrylic acids. It was converted into the *anilide*, which crystallised from dilute alcohol or, better, from petroleum (b. p. 60—80°) in fine needles, m. p. 88° (Found : C, 76·0; H, 8·2. $C_{12}H_{15}ON$ requires C, 76·2; H, 8·0%).

The *anilide* of αββ-trimethylacrylic acid, prepared for comparison, was similar in appearance but had m. p. 94°; a mixture of the two melted at 78—80°.

The oil produced by boiling the liquid acid with 64% aqueous potassium hydroxide for a few minutes and acidifying the cooled solution solidified slowly and was identified as αββ-trimethylacrylic acid by direct comparison with a genuine specimen.

Ethyl cyclo*Pentylidenemalonate* (V).—Attempts to condense ethyl malonate with *cyclo*pentanone by means of tertiary bases were unsuccessful. With sodium ethoxide, a small amount of the corresponding acid was produced (see below).

Ethyl malonate (80 g.), 42 g. of *cyclo*pentanone, 50 c.c. of acetic anhydride, and 30 g. of zinc chloride were heated together on the steam-bath for 70—80 hours. The black mixture was poured into water and extracted with ether, and the extract was washed until the washings were colourless. The dried extract was evaporated and distilled, some 11 g. boiling at 136—144°/10 mm.; this fraction gave with ferric chloride a slight coloration, due to the presence of an impurity which could be removed by extraction with 15% aqueous potassium hydroxide. The purified ester, b. p. 140°/10 mm., consisted of *ethyl* cyclo*pentylidenemalonate* (Found: C, 63·4; H, 8·1. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·1%).

A much better yield of the ester was obtained by using the double compound of aniline and zinc chloride in the place of zinc chloride: 60 c.c. of aniline were gradually added to 150 g. of powdered zinc chloride and the mixture was well stirred; the solid was then added to 480 c.c. of ethyl malonate, 264 c.c. of *cyclo*pentanone, and 360 c.c. of acetic anhydride, and the whole heated and worked up as before. On distillation, the highest fraction contained a quantity of acetanilide which could be removed by the addition of light petroleum; the final yield was 195 g., b. p. 145—160°/20 mm. With zinc chloride–aniline alone, very little condensation takes place. An attempt was made to synthesise the ester from 1-chloro-Δ^1-*cyclo*pentene and ethyl sodiomalonate, but no reaction took place.

The ester was hydrolysed by 30% aqueous potassium hydroxide and a few drops of alcohol. cyclo*Pentylidenemalonic acid*, isolated in the usual way, readily solidified and crystallised from ethyl acetate–petroleum in rectangular prisms and from hydrochloric acid in plates, m. p. 169° (decomp.) (Found: C, 56·4; H, 5·9. $C_8H_{10}O_4$ requires C, 56·4; H, 5·9%. Titration: Found, 20·2 c.c. of *N*/20-NaOH. Calc. for a dibasic acid, 20·15 c.c.).

Oxidation. *cyclo*Pentylidenemalonic acid was dissolved in sodium hydrogen carbonate solution, and a slight excess of 1% potassium permanganate solution added. The acid products were isolated in the usual way and converted into their calcium salts; calcium oxalate then separated. From the filtrate, strongly acidified with

hydrochloric acid, ether extracted glutaric acid, which was identified by comparison with a genuine specimen.

The pure acid (2·8 g.) was dissolved in chloroform and treated with ozone. The ozonide was decomposed by dilute sulphuric acid, and distillation in steam then gave *cyclo*pentanone, which was isolated in the form of its semicarbazone (1 g.); the residue contained a considerable amount of oxalic acid. *cyclo*Pentanone was also obtained by decomposing the ozonide of the ester.

A pure specimen of ethyl *cyclo*pentylidenemalonate was prepared by the action of ethyl iodide on the silver salt of the acid suspended in ether. It boiled at 139—141°/10 mm. and had $d_4^{19\cdot8°}$ 1·06164, $n_D^{19\cdot8°}$ 1·47241, $[R_L]_D$ 59·59 (calc., 58·02). On ozonisation and subsequent decomposition it gave *cyclo*pentanone; it had, therefore, the same structure as the ester obtained by direct condensation.

Methylation. The ester was twice treated with sodium methoxide and methyl iodide under the usual conditions. The ester isolated was hydrolysed to the *acid*, which solidified at once and crystallised from ethyl acetate and benzene in clusters of needles, m. p. 136·5° (decomp.), and from water in plates (Found: C, 58·6; H, 6·6. $C_9H_{12}O_4$ requires C, 58·7; H, 6·6%. Titration: Found, 19·1 c.c. of *N*/20-NaOH. Calc. for a dibasic acid, 19·1 c.c.). The acid was re-esterified through the silver salt, the *ester* (IX) having b. p. 150°/20 mm., $d_4^{22\cdot0°}$ 1·03457, $n_D^{22\cdot0°}$ 1·45853, $[R_L]_D$ 63·24 (calc., 62·64) (Found: C, 64·8; H, 8·4. $C_{13}H_{20}O$ requires C, 65·0; H, 8·4%).

The methylated ester was ozonised in moist chloroform solution, and the ozonide decomposed with dilute sulphuric acid; no products volatile in steam were obtained. The thick oil remaining after steam distillation had the properties both of an aldehyde and of an acid, giving a semicarbazone, m. p. 165° after crystallisation from alcohol; it gave glutaric acid on further oxidation, even by air, and therefore was the semialdehyde of glutaric acid.

The methylated ester (7 g.) was kept at 35° with an excess of alcoholic sodium ethoxide for several hours. Water was then added, the oil extracted with ether, and the extract distilled. A low fraction was obtained, consisting of ethyl carbonate; 1·5 g. of a middle fraction, b. p. 95—105°/10 mm., which was somewhat impure ethyl α-Δ^1-*cyclo*pentenylpropionate (Found: C, 72·7; H, 9·6. Calc.: C, 71·4; H, 9·5%); and a high fraction of unchanged ester, which was identified by hydrolysis to the acid.

The ester (V) was treated in the same way, but was recovered unchanged.

Addition of hydrogen cyanide, ethyl acetoacetate, and ethyl cyanoacetate. The pure ester (V) (22·6 g.) was kept for 10 days with 15 g. of potassium cyanide in 60 c.c. of water and 125 c.c. of alcohol.

The solution was filtered from a small amount of solid, diluted with water, acidified with hydrochloric acid, and extracted with ether. The extract yielded a viscous oil which gave scarcely any low fraction on distillation; 10 g. were obtained boiling at 200—210°/10 mm. This product was hydrolysed by 20 c.c. of sulphuric acid and 8 c.c. of water. Much charring occurred, but a quantity of 1-carboxy*cyclo*pentane-1-acetic acid, m. p. 156°, was isolated; it was identified by comparison with a genuine specimen.

The ester (V) did not condense with ethyl sodioacetoacetate. It was treated with ethyl cyanoacetate and alcoholic ammonia (Kon and Thorpe, J., 1919, **115**, 686). After 3 days the product was worked up as usual and the *imide* (VII), forming small prisms, m. p. 163°, from alcohol, was obtained in 42% yield (Found: C, 58·9; H, 6·2; N, 10·8. $C_{13}H_{16}O_4N_2$ requires C, 59·1; H, 6·1; N, 10·6%). The imide was hydrolysed by 70% sulphuric acid, giving a good yield of *cyclo*pentane-1 : 1-diacetic acid, m. p. 176—177°.

Ethyl Δ^1-cyclo*Hexenylmalonate* (VI).—This substance was prepared from *cyclo*hexanone by the method used for the preparation of (V). The yield was about the same in the two cases. The ester so obtained gave high figures for carbon on analysis and could not be completely purified by distillation. It was therefore hydrolysed by potassium hydroxide (see p. 2731) to the *acid*, which was readily obtained solid and crystallised in prisms, m. p. 150° (decomp.), from ethyl acetate and petroleum or from hot water (Found: C, 58·7; H, 6·7. $C_{19}H_{12}O_4$ requires C, 58·7; H, 6·6%. Found for the silver salt: Ag, 54·5. $C_{19}H_{10}O_4Ag_2$ requires Ag, 54·2%). When the acid was melted and the residue distilled under reduced pressure, Δ^1-*cyclo*hexenylacetic acid was produced.

The acid, m. p. 150°, was esterified through the silver salt and pure *ethyl* Δ^1-cyclo*hexenylmalonate* was thus readily obtained, b. p. 160°/20 mm., $d_4^{22·5°}$ 1·04419, $n_D^{22·5°}$ 1·46470, $[R_L]_D$ 63·42 * (calc., 62·64). The esterification was also carried out in the cold by means of alcohol and sulphuric acid, but a large fraction of low b. p., evidently ethyl *cyclo*hexenylacetate, was obtained, the yield of ester (VI) being only 40%; this boiled at 160°/20 mm. on redistillation (Found: C, 64·9; H, 8·5. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%) and had $[R_L]_D$ 63·27. Esterification by boiling the acid with alcohol saturated with hydrogen chloride gave an 80% yield of ester with 20% of low fraction.

Attempts to prepare the ester (VI) by other methods. The condensation of ethyl sodiomalonate with 1-chloro*cyclo*hexene was unsuccessful. Ethyl α-bromo*cyclo*hexylmalonate (Hope and Perkin,

* The value is practically identical with that for ethyl α-methyl-α-Δ^1-*cyclo*pentenylmalonate (p. 2732).

J., 1909, **95**, 1363) was boiled with diethylaniline and with pyridine, but the product in each case was ethyl *cyclo*hexylmalonate, which was readily identified by hydrolysis to the corresponding acid, m. p. 176°; with diethylamine, a part of the bromo-ester remained unchanged. Attempts to remove bromine from α-bromo*cyclo*hexylmalonic acid, and to hydrolyse α-cyano*cyclo*hexylideneacetic acid (Harding, Haworth, and Perkin, J., 1908, **93**, 1949) to the dicarboxylic acid by means of sulphuric acid, were unsuccessful.

Oxidation of the ester (VI). The pure ester was ozonised in chloroform, the ozonide boiled with dilute sulphuric acid, and the product distilled in steam; Δ^1-*cyclo*pentenyl methyl ketone (Harding, Haworth, and Perkin, *loc. cit.*) was obtained in considerable quantity and characterised by its semicarbazone, m. p. 203—204° (Found: C, 57·5; H, 8·2. Calc.: C, 57·5; H, 7·8%); no trace of *cyclo*hexanone appeared to be produced. Ozonisation of the acid and of the ester obtained by direct condensation gave the same result, and oxidation of the acid by permanganate yielded adipic acid.

Methylation. The ester (VI) was methylated twice in the same way as the ester (V). The *ester* (X), obtained in 80% yield, was hydrolysed to the *acid*, which crystallised from ethyl acetate and benzene in clusters of needles, m. p. 155° (decomp.) (Found: C, 60·9; H, 7·2. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1. Titration: Found, 18·95 c.c. of *N*/20-NaOH. Calc. for a dibasic acid, 18·85 c.c.). On re-esterifying the acid through its silver salt, the pure ester (X) was obtained, b. p. 152—154°/16 mm., $d_4^{19·8°}$ 1·03723, $n_D^{19·8°}$ 1·46748, $[R_L]_D$ 68·06 (calc., 67·26) (Found: C, 66·1; H, 8·9. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%). The methylated ester was treated with sodium ethoxide as described on p. 2732, but, like the parent ester, was recovered unchanged.

Addition of hydrogen cyanide, ethyl acetoacetate, and ethyl cyanoacetate. No condensation products could be obtained with the first two reagents. With ethyl cyanoacetate and ammonia, no condensation occurred when the pure ester, prepared through the silver salt, was employed. With all other samples of the ester, a poor yield (about 10%) of the ω-imide of αα′-dicyano*cyclo*hexane-1 : 1-diacetic acid was obtained (Guareschi, *Atti R. Accad. Sci. Torino*, 1911, **46**, 662). The unchanged ester recovered from the condensation could not be condensed again. Attempts were also made to condense the ester with ethyl sodiocyanoacetate, but no recognisable products could be isolated, although the higher-boiling fractions of the neutral oil appeared to consist of ethyl α-cyano-*cyclo*hexylideneacetate; they contained nitrogen and readily condensed with ethyl cyanoacetate and ammonia.

Our thanks are due to the Royal Society and to the Chemical Society for grants which have defrayed the cost of this investigation.

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CCCLXII.—*The Chemistry of the Three-carbon System. Part VIII. Tautomeric Systems terminated by a Phenyl Group.*

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THE tautomeric substances described in the earlier papers of this series have without exception the general structure :

$$\underset{\alpha\beta\text{-Phase.}}{R{-}CH[H]{-}CR^1{=}\overset{|}{C}{-}X} \rightleftharpoons \underset{\beta\gamma\text{-Phase.}}{R{-}CH{=}CR^1{-}\overset{|}{C}[H]{-}X}$$

where R, R^1 are positive groups—alkyl groups or portions of an alicyclic ring—and X is a negative activating group containing one or more double or triple bonds. The $\alpha\beta$-phase is stabilised by conjugation with these double or triple bonds, the $\beta\gamma$-phase by the decrease in strain or free energy which appears to be brought about by the introduction of a double bond into certain branched chains. The substances investigated have been those in which the two phases have approximately equal stabilities and in which the activating force has been sufficient to produce mobility.

Tautomeric substances are also known in which mobility in the system is induced by negative substituents at both ends of the three-carbon chain, *e.g.*, the glutaconic acids and esters and their cyano- and carbethoxy-derivatives. Many of these molecules are sufficiently symmetrical for the occurrence of semi-aromatic or normal structure (Thorpe, J., 1905, **87**, 1670). Little systematic work has, however, been carried out on negatively substituted systems in which there is no such symmetry and in which the tautomerism is of the type described in the earlier papers of this series. It is with the object of increasing such knowledge that a number of propene systems terminated by a phenyl group have been studied.

The presence of a substituent phenyl group in a three-carbon system should not in itself cause mobility, as it now appears that this is connected with the ability of the mobile hydrogen to leave the system temporarily and pass into the activating group. This consideration provides an explanation for the static nature of the

$\alpha\gamma$-diphenylpropenes (Ingold and Piggott, J., 1922, **121**, 2381). On the other hand, the double bond of a substituent side-chain should show a strong tendency to become conjugated with the double bonds of a benzene nucleus—numerous examples of this phenomenon have been recorded—and therefore the phenyl group, if properly placed, should produce a marked effect on the position of equilibrium in the three-carbon system.

Examples of this effect are found in the γ-phenylbutenoic acids, styrylacetic acid * (I) and γ-phenylcrotonic acid (II), which are two distinct, crystalline substances.

(I.) $CHPh{:}CH{\cdot}CH_2{\cdot}CO_2H$ $\qquad$ $CH_2Ph{\cdot}CH{:}CH{\cdot}CO_2H$ (II.)

These were first examined in detail by Fittig and his collaborators (*Annalen*, 1882, **216**, 97, 115; 1894, **283**, 297), who showed that in the presence of sodium hydroxide an equilibrium mixture of the two acids together with the corresponding β-hydroxy-acid was formed. The equilibrium was abnormal, however, in that there was present only a very small amount of the $\alpha\beta$-acid (II). Styrylacetic acid has since been made from phenylacetaldehyde by Vorländer (*Annalen*, 1906, **345**, 244) and by Fichter and Latzko (*J. pr. Chem.*, 1906, **74**, 327), using the Döbner method. As a result of many experiments we find that the acid is best made by condensing phenylacetaldehyde in alcoholic solution with malonic acid, a small amount of diethylamine being used as condensing agent. The acid product is exclusively styrylacetic acid; no substituted malonic acids nor any γ-phenylcrotonic acid can be detected, but some ethyl styrylacetate can be isolated from the neutral product of the reaction.

The action of sodium hydroxide on the acid under more vigorous conditions than those of Fittig (*loc. cit.*) has been investigated. The action of 40 times the theoretical amount of the alkali in 20% solution produced a mixture of 0·5% of the $\alpha\beta$-acid, 10% of the β-hydroxy-acid (V), 50% of unchanged $\beta\gamma$-acid, and a trace of lactone. Allowance being made for the recovery of unchanged acid, the yield of the hydroxy-acid is about 26%. Fittig, using 10 times the theoretical amount of 20% alkali, obtained less than 1% of the $\alpha\beta$-acid and a little more than this amount of the β-hydroxy-acid. In our experiments, the time of boiling was 100 hours as against the 20 to 80 hours of Fittig.

With a view to determine the effect of the phenyl group on the

* We have followed Beilstein ("Organische Chemie," 4th edn., vii, 293) in using the name "styrylacetic" in the place of "phenyl*iso*crotonic" for the acid (I), as the older name implies a structural relationship with crotonic acid which does not exist. Other compounds in the series have been named correspondingly.

mobility of the system, the action of sodium ethoxide on ethyl styrylacetate was investigated. An orange colour was produced immediately, but no definite proof of the formation of a sodio-derivative has yet been obtained, nor has the ester been alkylated. The ester can be condensed with ethyl sodioacetoacetate to give the sodio-derivative of the ester (III), which passes on hydrolysis into 3 : 5-diketo-1-benzyl*cyclo*hexane (IV). In the presence of sodium ethoxide, therefore, the ester becomes mobile and the αβ-phase then condenses with ethyl sodioacetoacetate in the usual way.

$$\begin{matrix} \mathrm{CHPh{:}CH{\cdot}CH_2{\cdot}CO_2Et} \\ \vdots\quad\vdots \\ \mathrm{CH_2Ph{\cdot}CH{:}CH{\cdot}CO_2Et} \end{matrix} + \mathrm{CO_2Et{\cdot}CHNa{\cdot}CO{\cdot}CH_3}$$

$$\longrightarrow \text{(III.)}\ \begin{matrix} \mathrm{CH_2Ph{\cdot}CH{\cdot}CH{:}C{\cdot}OH} \\ \mathrm{CO_2Et{\cdot}CH{\cdot}CO{\cdot}CH_2} \end{matrix} \longrightarrow \begin{matrix} \mathrm{CH_2Ph{\cdot}CH{\cdot}CH_2{\cdot}CO} \\ \mathrm{CH_2{\cdot}CO{\cdot}CH_2} \end{matrix} \text{(IV.)}$$

In these additive reactions, the ester is unique among βγ-butenoic esters : even ethyl Δ^1-*cyclo*hexenylacetate fails to give addition products under similar conditions.

For comparison with the ester, the corresponding ketone, ***styryl-acetone*** (V), was prepared. The phenyl ketone (VI) has been synthesised by Wieland and Stenzel (*Ber.*, 1907, **40**, 4825), who showed that it readily enolises and that the methylene group

(V.) $\mathrm{CHPh{:}CH{\cdot}CH_2{\cdot}CO{\cdot}CH_3}$ $\mathrm{CHPh{:}CH{\cdot}CH_2{\cdot}COPh}$ (VI.)

condenses with benzaldehyde, both reactions indicating the presence of a mobile hydrogen atom.

The condensation of phenylacetaldehyde with acetone by means of sodium methoxide, aqueous sodium hydroxide, aqueous potassium cyanide, or alcoholic potassium hydroxide failed to give the ketone (V), and its condensation with ethyl acetoacetate, with diethylamine or sodium ethoxide as condensing agent, led to the production of high-boiling gums. The ketone was readily prepared, however, by the action of zinc methyl iodide on styrylacetyl chloride, its structure thus being proved, and the βγ-position of the double bond was confirmed by its oxidation to benzaldehyde. It reacted immediately with sodium in alcohol, giving a deep red solution. Attempts to alkylate it either in alcoholic or in ethereal solution (compare Kon, this vol., p. 1792) led to the production of high-boiling gums.* In the course of one such alkylation, however, an interesting side reaction was observed. The reaction was carried out in the usual way in a flask open to the air and a 30% yield of

* The production of gums and resins in the course of this work was probably due in many instances to fission of the compounds at the double bond followed by auto-condensation of the aldehydes so formed.

styrylacetic acid was obtained in addition to the neutral products. This curious example of aërial oxidation is unique in our experience, although many similar experiments have been performed with ketones of this type. The ethyl iodide used, which had been made by the phosphorus method, contained a sub-analytical trace of a strongly odorous phosphorus compound. As the ethylphosphines are known to absorb oxygen readily from the air, this may possibly have been the active catalytic agent.

The ketone (V) resembles the corresponding ester in that the equilibrium mixture formed by the action on it of sodium ethoxide adds on ethyl sodiomalonate very readily with the formation of the resorcinol ester (III) already prepared from the ester, together with its sodio-derivative. The structures of these two substances were shown by their hydrolysis to diketobenzyl*cyclo*hexane (IV), which was identical with the compound previously obtained.

It was obviously of great interest to prepare the αβ-isomerides of styrylacetic acid and styrylacetone. The αβ-acid, γ-phenylcrotonic acid (II), can be prepared only in minute quantities, either by the action of sodium hydroxide on the βγ-acid or from the β-hydroxy-acid (VII) by dry distillation; it is also formed to the almost complete exclusion of styrylacetic acid by the action of acetic anhydride on the β-hydroxy-acid. The product is identical with Fittig's acid in its properties and gives phenylacetaldehyde on oxidation with permanganate.

(VII.) $CH_2Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$ $CH_2Ph{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$ (VIII.)

$CH_2Ph{\cdot}CH_2{\cdot}CBr(CO_2H)_2$ (IX.)

Attempts to prepare the acid by the action of secondary bases on either of the acids (VIII) and (IX) gave γ-phenylbutyric acid as the sole product (compare Hope and Perkin, J., 1909, **95**, 1360).

We have therefore been unable to develop a more successful method for the preparation of γ-phenylcrotonic acid than that from the β-hydroxy-acid already mentioned, and with the small quantity of material available our experiments were confined to an observation of the effect of alkali on the acid. When the acid was treated with an excess of 10% sodium hydroxide solution in the cold, styrylacetic acid was formed in good yield and no other acid could be isolated.

The next substance investigated was ethyl α-cyano-α-styrylacetate (X), which provided an interesting contrast with ethyl α-cyano-*cyclo*hexylideneacetate, from which it differs in that it normally has the βγ-structure. Like the *cyclo*hexylidene ester, however, in the presence of alcoholic ammonia it gives good yields of addition products derived from the αβ-form.

The ester (X) was first synthesised by Haworth (J., 1909, **95**, 482), who showed that the α-hydrogen atom could be replaced by sodium and that the sodio-derivative thus formed reacted with ω-bromoacetophenone to give the substance (XI). In addition, the cyano-ester (X), in the presence of alkali, added on water at the double bond to give, finally, the cyano-lactone (XII).

(X.) $CHPh{:}CH{\cdot}CH(CN){\cdot}CO_2Et$

(XI.) $CHPh{:}CH{\cdot}C(CN){\cdot}CO_2Et$
$\quad\quad\quad

only to phenylacetic acid, and not, by oxidation of the side chain, to benzoic acid under the same conditions.

It was impossible to prove or disprove the presence of a small quantity of the αβ-isomeride by oxidation, but that such a trace was present, and, in short, that the substance is an equilibrium mixture containing a large proportion of the βγ-form, was shown very clearly by the following experiment. When ethyl α-cyanostyryl-acetate was treated with alcoholic ammonia and ethyl cyanoacetate in the cold, addition to the αβ-phase readily occurred with the production of α-cyano-γ-phenylbutyramide (XV) and 3 : 5-dicyano-6-hydroxy-4-benzyl-2-pyridone (XVI), the latter being isolated in the form of its mono-ammonium salt. These had been formed from cyanostyrylacetamide (XIII) and the dihydropyridone (XIV) by a process of auto-oxidation and reduction similar to that found by Guareschi (*Atti R. Accad. Sci. Torino*, 1898—1899, **34**, 565) and Day and Thorpe (J., 1920, **117**, 1466).

$CHPh{:}CH{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$ (XIII.) $CH_2Ph{\cdot}CH_2{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$ (XV.)

(XIV.) $CH_2Ph{\cdot}CH\langle \begin{matrix} CH(CN){\cdot}C{\cdot}OH \\ CH(CN){\cdot}CO \end{matrix} \rangle N$ $CH_2Ph{\cdot}C\langle \begin{matrix} CH(CN){\cdot}C{\cdot}OH \\ C(CN)-CO \end{matrix} \rangle N$ (XVI.)

The pyridone (XVI) resembles other substances in the same group in not giving a glutaconic or glutaric acid on hydrolysis with sulphuric acid.

The sodio-derivative of ethyl cyanostyrylacetate reacts in alcoholic solution with methyl iodide to form the corresponding α-methyl ester. This loss of the mobile hydrogen atom is followed by elimination of the carbethoxy-group with the formation of a methylated nitrile, probably having the formula

$$CHPh{:}CH{\cdot}CHMe{\cdot}CN,$$

and ethyl carbonate. This reaction is in accordance with previous observations on the subject (Rogerson and Thorpe, J., 1905, **87**, 1702; Ingold and Thorpe, J., 1919, **115**, 143; Birch, Kon, and Norris, J., 1923, **123**, 1369).

This nitrile and related compounds are readily converted into naphthalene derivatives—a transformation which will be discussed in a future paper. Ethyl α-cyanostyrylacetate itself does not form a naphthalene derivative when treated with cold concentrated sulphuric acid; addition of water to the double bond occurs, followed by hydrolysis and lactone formation. The final product is a cyano-lactone apparently identical with that (XII) isolated by Haworth (*loc. cit.*).

In general, this investigation shows that the chief effect of the

γ-phenyl group is to confer an unusual degree of stability on the double bond in the βγ-position. The fact that ethyl α-cyano-α-styrylacetate exists almost completely in the βγ-phase shows that in its attraction for a double bond the phenyl group is stronger than the very powerful cyano-ester group. If the β-carbon as well as the γ-carbon atom in the propene system carries a phenyl group, this effect is lost; *e.g.*, in βγ-diphenylcrotonic acid (Fichter, *loc. cit.*) and in βγ-diphenylcrotonolactone (Thiele, *Annalen*, 1901, **319**, 196).

Experimental.

Styrylacetic Acid (*γ-Phenyl-Δ$^{\beta}$-butenoic Acid*) (I).

A solution of malonic acid (50 g.), phenylacetaldehyde * (60 g.), and 10 drops of diethylamine in 130 c.c. of absolute alcohol was boiled under reflux for 6 hours; the product was poured into an excess of 2*N*-sodium carbonate and extracted with ether. The acid that crystallised from the acidified aqueous solution was recrystallised from water or light petroleum. It melted at 87° and did not depress the m. p.s of samples prepared by the methods of Jayne and Fittig (*loc. cit.*) and Fichter and Latzko (*loc. cit.*) (Found: C, 74·4; H, 6·2. Calc.: C, 74·0; H, 6·2%). The yield was 60%, but was sometimes lower owing to partial esterification. Changes in solvent, concentration, or duration of heating led to decreased yields.

The condensation of ethyl bromoacetate with phenylacetaldehyde was attempted by various methods with a view to preparing the β-hydroxy-acid corresponding to styrylacetic acid. The use of magnesium or zinc in benzene, or of zinc in ether as condensing agents led alike to the formation of high-boiling gums.

Potassium styrylacetate forms white plates, m. p. 245° (decomp.), from a concentrated aqueous solution (Found: K, 19·3. $C_{10}H_9O_2K$ requires K, 19·5%).

Styrylacetyl chloride, formed by the action of thionyl chloride on the acid, readily solidified on removal of the excess of the reagent. It crystallised from light petroleum in clusters of flattened needles, m. p. 42° (Found: Cl, 19·9. $C_{10}H_9OCl$ requires Cl, 19·6%). On treating it with anhydrous formic acid, the parent acid is re-formed.

Ethyl styrylacetate was formed as a by-product in the preparation of the acid and was isolated from the ethereal extract. The amount of esterification depended directly on the time of reaction. After refractionation, the product had optical properties in good agree-

* In this and other condensations the best yield is obtained when the phenylacetaldehyde has been freshly distilled. The aldehyde polymerises on standing, but may be kept in ethereal solution for a month or more with but little change.

ment with those obtained for the pure ester (see below) and its identity was confirmed by oxidation with ozone in chloroform solution and by hydrolysis. By decomposition of the ozonide with water followed by distillation in steam from an acid medium, benzoic acid was obtained. Hydrolysis of the ester with 50% aqueous potassium hydroxide gave potassium styrylacetate, from which the acid, m. p. 86—87°, was obtained.

The pure ester was prepared in excellent yield by esterifying the acid in the presence of sulphuric acid, or through the acid chloride. It had b. p. 164—165°/25 mm. and 184°/44 mm., $d_4^{20\cdot5°}$ 1·0340, $n_D^{20\cdot5°}$ 1·53271, $[R_L]_D$ 56·73 (calc., 55·21, Brühl's value for C_6H_5, 25·21, being used). It gave no colour with alcoholic ferric chloride (compare Vorländer, *loc. cit.*), an immediate red colour with sodium ethoxide, and an orange colour with "molecular" sodium in ether.

Action of Sodium Hydroxide on Styrylacetic Acid.—The method was essentially that of Fittig (*Annalen*, 1894, **283**, 297), but the conditions were more drastic, styrylacetic acid being boiled with 20% sodium hydroxide solution (40 times the quantity necessary for neutralisation) for 100 to 110 hours. In a typical experiment, 50 g. of styrylacetic acid gave 6 g. of the hydroxy-acid and 4 g. of mixed unsaturated acids, 23 g. of styrylacetic acid being recovered unchanged. The β-hydroxy-γ-phenylbutyric acid (VII) formed needles from the carbon disulphide solution and had m. p. 96°. The unsaturated acids in the filtrate from the hydroxy-acid were freed from carbon disulphide and, on standing, yielded a small quantity of styrylacetic acid. The oily residue was converted into barium salts which, on fractional crystallisation from water, gave the powdery salt of styrylacetic acid and 2 g. of a gummy salt. The latter, on acidification, gave a mixture of the βγ-acid (needles, m. p. 84°) and the αβ-acid (plates, m. p. 58°) in about equal quantities. The yield of αβ-acid was 0·8 g. The loss (about 40%) was due mainly to the formation of resinous material.

γ-Phenylcrotonic acid was also produced when β-hydroxy-γ-phenylbutyric acid (10·6 g.) was boiled under reflux with acetic anhydride (20 c.c.) for 3 hours. The bright red, heavy product was boiled in a current of steam until it was free from acetic acid. The residue was extracted with ether, the extract dried, and the ether removed. The residual oil was converted in the usual way into a gummy barium salt, which was dried in a vacuum desiccator (yield, 9 g.). A hot, filtered, aqueous solution of the salt, on acidification and cooling, deposited crystals of phenylcrotonic acid, and more were obtained on concentrating the mother-liquor. After complete evaporation, the semi-solid residue was drained on porous tile, more phenylcrotonic acid being thus obtained (total yield, 2 g. or 21%).

γ-Phenylcrotonic acid forms white, shimmering leaflets, m. p. 58—59°, from water (Fittig gives 65°). The melting point of a mixture with the 87°-acid is much lower. On oxidation with alkaline permanganate the acid gives phenylacetaldehyde. The acid chloride, made by means of thionyl chloride, is a liquid which does not solidify in a freezing mixture.

3 : 5-*Diketo*-1-*benzyl*cyclo*hexane* (IV).—Pure ethyl styrylacetate (b. p. 164—165°/25 mm.) (9·5 g.) was added to ethyl sodioacetoacetate prepared from 6·5 g. of acetoacetic ester and 1·15 g. of sodium in 15 c.c. of ethyl alcohol. The red solution was boiled under reflux for 4 hours, becoming almost completely solid, and thereafter heated on the steam-bath for 12 hours. The solid sodium derivative was filtered off (6·5 g.), and the filtrate freed from alcohol by suction. The semi-solid residue was dissolved in water and extracted with ether, but only a small quantity of the ester (III) was thus obtained. From the neutral fraction 1·5 g. (= 16%) of ethyl styrylacetate were recovered. Allowance being made for this, the yield of the sodium derivative was 55%.

On treatment with hydrochloric acid, the sodium derivative gave an oily ester (III), which developed a purple coloration in presence of alcoholic ferric chloride. The sodium derivative (6·5 g.) was boiled with a solution of 30 g. of sodium carbonate crystals in 18 c.c. of water for 20 hours, carbon dioxide and alcohol being freely evolved. The brown solution was acidified with hydrochloric acid and exhaustively extracted with ether. From the dried extract a gum was obtained which readily solidified on being rubbed with a little cold ether. It was recrystallised from boiling ether with the aid of animal charcoal (yield, 2 g. or 46%). When hydrolysed under these conditions, the ester (III) yielded the same product.

3 : 5-*Diketo*-1-*benzyl*cyclo*hexane* (IV), thus obtained, forms glistening plates, m. p. 118°. It is insoluble in water, light petroleum, or chloroform, soluble in alcohol, acetone, or hot ether, and sparingly soluble in cold ether (Found : C, 77·6; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). It gives a much weaker colour with ferric chloride than the corresponding ester (III), it resinifies readily in contact with hydrolytic solvents, and dissolves slowly but completely in sodium bicarbonate solution.

On boiling diketobenzyl*cyclo*hexane with baryta solution, ring fission occurred and a gummy acid was formed which could not be obtained pure. In this respect it resembles diketophenyl*cyclo*hexane (Vorländer, *Annalen*, 1897, **294**, 273).

Styrylacetone (V).

Styrylacetyl chloride was allowed to react with zinc methyl iodide as described in J., 1923, **123**, 1361. The acid product extracted by 10% sodium hydroxide solution consisted of a small amount of styrylacetic acid. The neutral product, after removal of benzene, was fractionated under reduced pressure, the new ketone being obtained, b. p. 145—165°/20 mm. (yield, 30 to 45%). The substitution of methyl acetate for ethyl acetate did not improve the yield.

Styrylacetone is a mobile liquid with a faint smell. It is pale yellow when freshly prepared, but the colour slowly deepens. It has b. p. 262°/75 mm., 150°/15 mm., and distils under normal pressure almost without decomposition. It gives no colour with ferric chloride.

The *semicarbazone* is very readily formed and crystallises from dilute alcohol in lustrous plates, m. p. 160° (Found : C, 66·2; H, 7·2. $C_{12}H_{15}ON_3$ requires C, 66·3; H, 7·0%). No second semicarbazone is formed.

The structure of the ketone was confirmed by oxidation with ozone. The ozonide was decomposed with water and the benzaldehyde produced was identified as the semicarbazone, m. p. 219—220°.

Action of Sodium Ethoxide on Styrylacetone.—(a) *Attempted alkylation.* The ketone (10 g.) was treated with 1·53 g. of sodium in 20 c.c. of absolute alcohol, moisture being carefully excluded. A red colour developed immediately, but it faded on the addition of ethyl iodide (6 c.c.). The mixture was worked up in the usual way. The neutral fraction gave a high-boiling gum (9 g.) and the acid fraction gave 3 g. of styrylacetic acid. The weights of the products indicated that alkylation had occurred, but although the experiment was repeated a number of times under various conditions, an alkylated ketone could not be isolated.

(b) *Formation of* 3 : 5-*diketo*-1-*benzyl*cyclo*hexane* (IV). Equimolecular quantities of styrylacetone and ethyl sodiomalonate were heated together in alcoholic solution for 16 hours; the mixture then partly solidified. The products were worked up as described on p. 2743. The yields were smaller, 25% of the sodium compound and 16% of the ester (III) being obtained. These were hydrolysed separately in the manner already described. The product in each case was 3 : 5-diketo-1-benzyl*cyclo*hexane. This was identified with the substance previously prepared from ethyl styrylacetate by its melting point, characteristic crystalline form, and by a mixed melting-point determination.

Experiments with ω-Bromostyrene.

ω-Bromostyrene, prepared by Nef's method (*Annalen*, 1899, **308**, 267), had b. p. 105°/17 mm. Attempts to condense it with the sodio-derivatives of ethyl malonate, acetoacetate, and cyanoacetate in alcoholic, benzene, or xylene solution failed.

Experiments on the Elimination of Hydrogen Bromide from α-Bromo-γ-phenylbutyric Acid and α-Bromo-α-(β-phenylethyl)malonic Acid.

β-Phenylethyl bromide was prepared in excellent yield by the action of 40% hydrobromic acid on β-phenylethyl alcohol in the presence of sulphuric acid. The heavy product, after being separated, washed, and dried, had b. p. 109°/22 mm. and 92°/11 mm.

The bromide was converted into α-bromo-α-(β-phenylethyl)-malonic acid (IX) by Fischer and Schmitz's method (*Ber.*, 1906, **39**, 2208). The bromo-acid crystallised from toluene in needles, m. p. 156°, and on distillation gave α-bromo-γ-phenylbutyric acid (VIII), b. p. 183°/9 mm., a liquid which did not solidify in a freezing mixture.

The bromophenylbutyric acid (7 g.) in ethereal solution was left in contact with an excess of diethylamine for a week. No bromine-free product could be isolated from the reaction mixture.

The bromomalonic acid (IX) (6·5 g.) was heated with pyridine (2 mols.) at 160—180° for ½ hour. The acid product, after being freed from pyridine and charred material, was recrystallised from hot water, shimmering leaflets, m. p. 50°, of γ-phenylbutyric acid, identified by the melting point of a mixture with a sample of the acid made by Fischer and Schmitz's method (*loc. cit.*), being obtained.

Ethyl α-Cyano-α-styrylacetate (X).

A mixture of phenylacetaldehyde and ethyl cyanoacetate (0·25 g.-mol. of each) was cooled in ice and, after 2·5 c.c. of diethylamine had been slowly added, left at room temperature for 24 hours or more. The viscous neutral product, after separation in the usual way, was fractionated under reduced pressure, the fraction, b. p. 180—202°/15 mm., being collected separately and refractionated.

Ethyl α-cyano-α-styrylacetate prepared in this way is fairly mobile when freshly distilled, but becomes viscous on standing. This is not, however, due to irreversible polymerisation, as the mobility is regained on redistillation. The pure ester has b. p. 192°/16 mm. (Haworth, *loc. cit.*, gives 195—197°/20 mm.), $d_4^{17.5°}$ 1·0912, $n_D^{17.5°}$ 1·53635, $[R_L]_D$ 61·22 (calc., 59·64). The yield obtained by this method varies from 25 to 32%, and compares favourably with that obtained by Haworth's method. If the reaction is carried out at 0°, the yield is lowered.

The product was identified with that prepared by Haworth by the formation of the ω-bromoacetophenone compound, which melted at 109—110° and did not depress the melting point of a sample prepared by Haworth's method.

When the condensation was carried out in presence of sodium ethoxide, a solid by-product was found in the neutral fraction of the condensate. This formed small plates, m. p. 220°, from acetic acid (Found : C, 81·3; H, 6·3. $C_{18}H_{17}ON$ requires C, 82·1; H, 6·5%). It was probably the hydroxy-nitrile,

$$CHPh{:}CH{\cdot}CH(CN){\cdot}CH(OH){\cdot}CH_2Ph,$$

formed by the action of a second molecule of phenylacetaldehyde on ethyl α-cyano-α-styrylacetate.

The ester (X) was stable to ozonised oxygen and to alkaline permanganate, but chromic acid broke the side chain at the double bond. The ester (2·1 g.) dissolved in glacial acetic acid (5 c.c.) was treated with three times the theoretical quantity of chromic acid in 20 c.c. of acetic acid. After ½ hour's heating, the solution was poured into 200 c.c. of water, cooled, and extracted with ether. The extract was freed from acetic acid by washing with water, dried, and evaporated, 1 g. of benzoic acid being thus obtained.

In a control experiment, phenylacetaldehyde (1 g.) in 5 c.c. of acetic acid was treated with 4 g. of chromic acid in 15 c.c. of acetic acid. The vigorous reaction was carried out as before and the products were worked up in the same way. The acid product was entirely phenylacetic acid, which was identified in the usual way.

The cyano-ester readily formed a sodio-derivative which reacted with ω-bromoacetophenone and with methyl iodide in alcoholic solution. (A description of the products obtained on methylation in alcohol will be given in a future paper.) Methylation in the presence of "molecular" sodium in ether led to the formation of Haworth's cyanolactone as the sole product. This compound was isolated as a resinous solid which could be crystallised with considerable difficulty from methyl alcohol and then melted at 85—90° (Found : N, 6·9. Calc.: N, 7·5%). The substance was readily soluble in alkali hydroxides and in ammonia solution. On boiling with 20% sodium hydroxide solution, ammonia was evolved. It appeared very probable that the substance was a mixture of two stereoisomeric forms, but no separation could be effected. The same substance was obtained in good yield by the action of cold concentrated sulphuric acid on ethyl α-cyano-α-styrylacetate, a reaction which confirms the structure assigned to it by Haworth.

Action of Ethyl Cyanoacetate and Ammonia on Ethyl α-Cyano-α-styrylacetate.—A mixture of ethyl cyanostyrylacetate (20·4 g.) and ethyl cyanoacetate (10·6 g.), cooled to 0°, was treated with

38 c.c. of absolute alcohol, previously saturated in a freezing mixture with ammonia. The mixture having been kept for 24 hours at 0°, the solid product was separated, washed with a little alcohol, and dried (yield, 14 g. or 55%). It was almost entirely the *mono-ammonium* salt of 3 : 5-*dicyano*-6-*hydroxy*-4-*benzyl*-2-*pyridone*, which crystallised from water in felted masses and from methyl alcohol in fine, white needles, charring without melting at 320° (Found : N, 20·4. $C_{14}H_{12}O_2N_4$ requires N, 20·9%). On treatment with hydrochloric acid 3 : 5-*dicyano*-6-*hydroxy*-4-*benzyl*-2-*pyridone* was obtained, which crystallised from dilute hydrochloric acid in lustrous leaflets, m. p. 279° (Found : C, 62·5, 62·6, 62·2; H, 5·0, 4·2, 4·2; N, 15·6. $C_{14}H_{11}O_3N_3$ requires C, 62·4; H, 4·1; N, 15·1%). It is readily soluble in hot water, alcohol, or benzene, insoluble in ether, and sparingly soluble in dilute acids and in acetic acid. The unsaturated nature of the 3 : 4-bond is confirmed by the fact that on hydrolysis of the pyridone with sulphuric acid under the conditions of Thole and Thorpe (J., 1911, **99**, 422) no β-benzylglutaric acid can be obtained, the product being a nitrogenous acid giving a fluorescent green solution in alkalis.

The viscous filtrate from the ammonium salt of the pyridone, when left in a vacuum desiccator, slowly deposited α-cyano-γ-phenylbutyramide contaminated with cyanoacetamide. In one experiment, 11 g. of the parent ester gave 4·6 g. of the cyanobutyramide and only a trace of cyanoacetamide. Usually, however, cyanoacetamide was present to the extent of more than 50% in this residue, from which it could be recovered by boiling with water.

α-*Cyano*-γ-*phenylbutyramide* (XV) crystallises from dilute methyl alcohol in shining, flattened needles, m. p. 151—152° (Found : C, 70·4; H, 6·5. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4%). It is considerably more soluble in alcohol than the other products of the reaction. It is insoluble in water and in alkalis, and does not decolorise permanganate.

We are indebted to the Government Grant Committee of the Royal Society and to the Chemical Society for grants which have partly defrayed the expense of the work, to Mr. C. Soyka of this College for assistance in the preparation of some of the materials, and to Professor J. F. Thorpe and Dr. G. A. R. Kon for their interest in the investigation.

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CCCLXIII.—*The Chemistry of the Three-carbon System. Part IX. The αβ–βγ-Change in β-Alkylcinnamic Acids.*

By JOHN DOBNEY ANDREW JOHNSON and GEORGE ARMAND ROBERT KON.

LINSTEAD and WILLIAMS (preceding paper) have shown that a terminal phenyl group, although capable of enhancing mobility when such is already present, cannot cause mobility in a three-carbon system, that is, cannot function as an activating group, because it is incapable of providing a point of attachment for a mobile hydrogen atom; it is, in fact, "non-polar." It has, however, a very powerful effect on the equilibrium of the system owing to the great tendency of double or triple linkings to become conjugated with its double linkings. For example, Stobbe (*Annalen*, 1902, **321**, 83; 1899, **308**, 67) obtained only the acid

$$CHPh{:}CPh{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$$

by condensing deoxybenzoin with ethyl succinate, the acid $CH_2Ph{\cdot}CPh{:}C(CO_2H){\cdot}CH_2{\cdot}CO_2H$ not being formed (compare also Fichter, *J. pr. Chem.*, 1906, **74**, 297).

A phenyl group in the β-position should not affect the *relative* stability of the αβ- and βγ-forms in a three-carbon system, because, being conjugated with the double bond in either form, it should exercise an equal stabilising influence on both forms. It is true that diphenylvinylacetic acid is said to be much less stable than its βγ-isomeride (Fichter, *loc. cit.*), but we do not attach much importance to this observation, especially as no proofs are given of the structure of the two acids.

These considerations led us to extend the work of Kon and Linstead (J., 1925, **127**, 616) on the αβ–βγ change to a series of β-phenyl compounds, including β-methyl-, ethyl-, propyl-, and *iso*propylcinnamic acids and their hitherto unknown βγ-isomerides. The αβ- and βγ-forms of β-ethylcinnamic acid, $CH_2Me{\cdot}CPh{:}CH{\cdot}CO_2H$ and $CHMe{:}CPh{\cdot}CH_2{\cdot}CO_2H$, are similar to the corresponding methylethylacrylic acids, except that in the former the double bond is conjugated with the phenyl group in both forms. These acids, therefore, should behave similarly under the influence of agents such as strong alkali—a prediction which it is proposed to justify experimentally. The results obtained by Stobbe (*loc. cit.*) on the acids $CH_2Me{\cdot}CPh{:}C(CO_2H){\cdot}CH_2{\cdot}CO_2H$ and

$$CHMe{:}CPh{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$$

are also in good agreement with this conception.

β-*Methylcinnamic acid*, $CPhMe{:}CH{\cdot}CO_2H$, the simplest member

of the series, is analogous to ββ-dimethylacrylic acid. The βγ-isomeride, $CH_2{:}CPh{\cdot}CH_2{\cdot}CO_2H$, is formed during the preparation of the αβ-acid,* but its presence has hitherto been overlooked owing to the small quantity (2%) produced: the oily by-product which is always formed when the αβ-acid is prepared by the hydrolysis of the ester (obtained by the dehydration of ethyl β-hydroxy-β-phenylbutyrate) is the βγ-acid (*β-phenylvinylacetic acid*) contaminated with the eutectic mixture of *cis*- and *trans*-β-methylcinnamic acids. Its structure is apparent from the fact that its ester gives formaldehyde on oxidation with ozone. The formation of this acid can be accounted for by the stabilising effect of the phenyl group on the double linking with which it is conjugated. It is rapidly converted into the stable αβ-acid by boiling concentrated alkali. Attempts have been made to prepare it from the αβ-acid by means of alkali, on the assumption that the two forms exist in equilibrium in presence of this reagent, but so far without success.

β-Ethylcinnamic Acids.—A totally different relationship is met with in the higher homologues. β-Ethylcinnamic acid,

$$CPhEt{:}CH{\cdot}CO_2H,$$

obtained by the hydrolysis of the corresponding unsaturated ester is always accompanied by a considerable quantity of an oil having the same composition. The two isomerides can be separated by the method used by Stoermer, Grimm, and Laage (*Ber.*, 1917, **50**, 966) for the separation of stable and *allo*-αβ-acids: the basic copper salt of the βγ-acid is insoluble in ether, so that mixtures of stable αβ- and βγ-acids can be separated into their constituents and their composition determined with considerable accuracy (to about 2%). The pure αβ-acid can be obtained by the action of acetic anhydride or cold concentrated sulphuric acid on the corresponding hydroxy-acid.

The oily acid is the *βγ-acid*, $CHMe{:}CPh{\cdot}CH_2{\cdot}CO_2H$; it gives acetaldehyde on oxidation with ozone and forms characteristic derivatives.

The action of alkali on either of the two acids gives an equilibrium mixture of the two isomerides, the proportions of which can be determined by the copper salt method; the results obtained with 50% potassium hydroxide solution are as follows (the figures indicate the compositions of the mixtures and not the yields from a given amount of acid, because fission, producing propiophenone [5%], always takes place):

Initial material.		αβ-Acid.			βγ-Acid.	
Duration of heating (hrs.)	1	2	4	1	2	4
% αβ-Acid formed	68	31	26	10	20	24

* Unless otherwise stated, the "αβ-acid" is the stable form in all cases.

Boiling with 50% sulphuric acid produces a somewhat similar effect, but the action is complicated by the formation of a lactone and of α-ethylstyrene; *e.g.*, after 1 hour's boiling the following are isolated :

	αβ-Acid.	βγ-Acid.	Lactone.	Hydrocarbon
From αβ-acid	60%	15%	5%	18%
From βγ-acid	22	49	12	17

The acid chlorides also undergo interconversion : on heating either chloride at 140—160° for 3 hours a mixture is obtained containing about 21% of the αβ-compound.

The mixture obtained by dehydrating ethyl β-hydroxy-β-phenylvalerate with phosphorus oxychloride or potassium hydrogen sulphate consists of the αβ- and βγ-esters.

β-*Propylcinnamic Acids.*—On hydrolysing the unsaturated ester produced by the dehydration of ethyl β-hydroxy-β-phenylhexoate a mixture of solid and liquid isomerides is again obtained. Schroeter (*Ber.*, 1908, **41**, 5) has suggested that the liquid may be the βγ-isomeride, but Stoermer, Grimm, and Laage (*loc. cit.*) have isolated from it the " misch form " (mixture of stable and *allo*-αβ-acids). This, however, forms only a very small proportion of the oil, from which we have isolated by the copper salt method a large quantity—about 50% of the original crude acid—of a liquid having the reactions of the βγ-acid, $CHEt{:}CPh{\cdot}CH_2{\cdot}CO_2H$. This was confirmed by oxidation of both the acid and its ester.

The two acids give the same amide, m. p. 100·5°, by Stoermer, Grimm, and Laage's method, and the same anilide, m. p. 108°, because the acid chloride produced by the action of phosphorus pentachloride on either acid is the βγ-derivative. The *anilide* of the αβ-acid has now been prepared and melts at 114°.

The interconversion of the two acids by different agents was investigated.

αβ-Acid.						
% Potassium hydroxide	10	10	10	50	50	50
Duration of heating (hrs.)	2¼	6	25¼	2	4	6
% αβ-Acid	60	53	53	54	52	53
βγ-Acid.						
% Potassium hydroxide	10	10	10	50	50	50
Duration of heating (hrs.)	2	6	24¼	2	4	6
% αβ-Acid	40	50	52	50	51	52

The change of concentration of the alkali from 10 to 50% affects only the rate at which equilibrium is established and not the final composition of the mixture.

On boiling the acids with 50% sulphuric acid, the following mixtures were produced :

	αβ-Acid.	βγ-Acid.	Lactone.	α-Propylstyrene.
From αβ-acid	53%	9%	5%	33%
From βγ-acid	8	38	7	47

On heating, the acid chlorides gave a mixture consisting of 46% αβ and 54% βγ. Attempts to produce isomerisation of the esters by the agency of sodium ethoxide were unsuccessful.

β-iso*Propylcinnamic Acids*.—These acids, neither of which had previously been prepared, have now been obtained from *iso*butyrophenone by the method employed in the preparation of the *n*-propyl acid and its βγ-isomeride, to which they bear a great resemblance. They were separated from each other, although with some difficulty, by the copper salt method.

The interconversion of the two acids was carried out by means of 50% potassium hydroxide solution; at the end of 6 hours a mixture containing 54% of the αβ-acid was obtained in each case. One hour's boiling with 50% sulphuric acid produced the following mixtures:

	αβ-Acid.	βγ-Acid.	Lactone.	α-*iso*Propylstyrene.
From αβ-acid	58%	6%	5%	31%
From βγ-acid	9	46	7	38

Reviewing the above results it will be seen that all the acids investigated have a degree of mobility greater than that of the corresponding aliphatic compounds. This increase in mobility is doubtless attributable to the influence of the phenyl group already discussed; nevertheless, none of the esters in this series could be alkylated. The second member of the series has a much greater tendency to pass into the βγ-form than either the propyl or the *iso*propyl compound. A possible explanation of this may be forthcoming as the result of further work on the influence of comparatively large groups on the position of equilibrium. The views already put forward regarding the position of equilibrium in unsaturated acids containing a *gem*-group have been materially strengthened by the outcome of the present work.

The preparation of the methyl ketones corresponding to the preceding β-alkylcinnamic acids is a matter of considerable difficulty, because the chlorides of the acids from which they can be synthesised show a great tendency to form equilibrium mixtures and the yields of ketone obtainable from them are poor. The two *ketones* corresponding to the ethylcinnamic acids, namely, $CH_2Me{\cdot}CPh{:}CH{\cdot}COMe$ and $CHMe{:}CPh{\cdot}CH_2{\cdot}COMe$, have been prepared. Although distinct, they readily form equilibrium mixtures in the presence of alcoholic alkalis, sodium ethoxide, or acids; they can also be ethylated, yielding the same ethyl derivative, which doubtless has

the structure $CHMe{:}CPh{\cdot}CHEt{\cdot}COMe$. The ketones are thus analogous to the ketones studied by Kon and Linstead (J., 1925, **127**, 814); but possess greater mobility, as they are readily alkylated. The ketone $CMePh{:}CH{\cdot}CO{\cdot}CH_3$ was prepared, but it was not possible to prepare the βγ-isomeride owing to the difficulty of obtaining the acid. The ketone has little tendency to pass into the βγ-form and cannot be alkylated.

None of the ketones or esters of this series undergoes the Michael reaction, owing, no doubt, to the inhibiting effect of the β-phenyl group.

Experimental.

β-Methylcinnamic and β-Phenyl-Δ$^{\beta}$-butenoic Acids.—Acetophenone was condensed with ethyl bromoacetate and magnesium in the usual way. The crude benzene solution of the hydroxy-ester was boiled with phosphorus oxychloride (⅓ mol.) for ½ hour, and the unsaturated ester isolated (Lindenbaum, *Ber.*, 1917, **50**, 1270). It had b. p. 142—145°/16 mm., $d_4^{19\cdot3^\circ}$ 1·04036, $n_D^{19\cdot3^\circ}$ 1·54510, $[R_L]_D$ 57·78 (calc., 55·20); the yield was 55% (Found: C, 75·6; H, 7·5. Calc.: C, 75·8; H, 7·4%). The ester was hydrolysed with 50% aqueous potassium hydroxide, enough alcohol being added to effect solution; a little acetophenone was produced together with the acid. The latter was twice extracted with hot petroleum (b. p. 40—60°), which left the greater part unattacked; the extract was concentrated somewhat and cooled; a small quantity of solid then crystallised. This, and also the solid undissolved by the petroleum, consisted of β-methylcinnamic acid, m. p. 98·5° (Found: C, 73·9; H, 6·2. Calc.: C, 74·1; H, 6·2%). Its solution in sulphuric acid was yellow.

The petroleum mother-liquors contained a quantity of the "misch form" (compare Stoermer, Grimm, and Laage, *loc. cit.*), m. p. 76°. The violet solution of this in sulphuric acid gradually became yellow; addition of water at this stage precipitated the pure stable acid, m. p. 98·5°. The most soluble constituent of the acid mixture consisted of the oily *βγ-acid* (*β-phenyl-Δ$^{\beta}$-butenoic acid*), which was still contaminated with a little of the "misch form" (Found: C, 73·8; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2%). The acids were present approximately in the following proportions: stable 89%, "misch form" 9%, βγ- 2%.

The *methyl* ester of the new acid, obtained by the action of methyl sulphate on the sodium salt (Stoermer, Grimm, and Laage, *loc. cit.*), had b. p. 138°/16 mm. (Found: C, 74·9; H, 6·8. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%); the αβ-ester has a somewhat higher b. p. The *anilide* was obtained in pearly plates, m. p. 127°; that of the stable αβ-acid has m. p. 121°. On treatment of the new ester with ozone

and decomposition of the ozonide, formaldehyde (identified by means of β-naphthol) was obtained; the non-volatile portion of the product, which reacted with copper acetate and gave a coloration with ferric chloride, was presumably methyl benzoylacetate.

The new acid, on boiling with an excess of 50% potassium hydroxide solution for 1 hour, was completely converted into β-methylcinnamic acid. The αβ-acid, subjected to the same treatment for 5 hours, was recovered unchanged.

The αβ-acid (10 g.) was boiled under reflux for 20 minutes, cooled, and extracted once with 50 c.c. of petroleum (b. p. 40—60°). The extract on concentration deposited about 1 g. of the " misch form "; the filtrate contained about 1 g. of α-methylstyrene, b. p. 160° (Found: C, 91·5; H, 8·6. Calc.: C, 91·5; H, 8·5%).

The αβ-acid (10 g.) was boiled for 1 hour with 50% sulphuric acid (100 c.c.), cooled, and extracted with ether. The extract was washed with sodium carbonate solution, which removed the αβ-acid; from the neutral portion, 2·3 g. of α-methylstyrene were isolated.

The chloride of the stable αβ-acid (b. p. 132°/18 mm.), prepared by means of thionyl chloride, remained unchanged on heating, and the pure acid could be regenerated from it.

β-Ethylcinnamic and β-Phenyl-Δ$^{\beta}$-pentenoic Acids.—The hydroxy-ester obtained from propiophenone by the Reformatski reaction in 35—40% yield had b. p. 152—154°/19 mm. It tended to lose water on distillation. The hydroxy-acid prepared from it had m. p. 123° after crystallisation from benzene; it was accompanied by small quantities of the unsaturated acids.

Stable β-ethylcinnamic acid was obtained from the hydroxy-acid by means of either cold concentrated sulphuric acid or boiling acetic anhydride and had m. p. 95° as found by previous authors.

allo-β-Ethylcinnamic acid was obtained from the above acid by the action of ultra-violet light, 62% being produced after 106 hours' exposure (Stoermer, Grimm, and Laage, *loc. cit.*). It was characterised by the formation of the anilide (needles, m. p. 122°).

β-Phenyl-Δ$^{\beta}$-pentenoic acid was produced when the hydroxy-ester was dehydrated by heating it for 3 hours with potassium hydrogen sulphate; the mixture of unsaturated esters obtained boiled at 152—159°/26 mm., and had $d_4^{17°}$ 1·0297 and $n_D^{17°}$ 1·52788. A more convenient method consists in treating the crude hydroxy-ester with phosphorus oxychloride as described on p. 2752. The products obtained by either of these processes gave propiophenone and acetaldehyde on oxidation with ozone and subsequent decomposition. On hydrolysis with potassium hydroxide, an oily mixture of acids was obtained which gave, on oxidation, products derived from

both the αβ- and the βγ-acid. By the basic copper salt method, the mixture was found to contain some 33% of the stable αβ-acid; this was identical with the acid prepared from the hydroxy-acid and gave propiophenone and oxalic acid on oxidation with permanganate (Found : C, 74·8; H, 6·9. Calc. : C, 75·0; H, 6·8%). The isomeric acid was liquid; on treatment with permanganate, it gave acetaldehyde, acetic and benzoic acids, and a trace of propiophenone * (Found : C, 74·9; H, 6·9%).

The *anilide* of the βγ-acid was obtained by heating the acid (1·96 g.) in dry ether with phosphorus pentachloride (2·48 g.) until the latter dissolved, cooling the mixture, and slowly adding an excess of aniline. The ethereal solution was shaken successively with dilute hydrochloric acid, alkali and water, dried, and evaporated; from the residue, crystallised from ether and light petroleum, rhombic plates were obtained, m. p. 127° (mixed m. p. with the *allo*-anilide, 94—99°) (Found : C, 81·2; H, 6·8; N, 5·6. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). The anilide of the stable αβ-acid obtained in the same way has m. p. 86° (Found : C, 81·1; H, 6·8; N, 5·7%). The anilides can also be obtained by treating an ice-cold solution of the acid and aniline in dry pyridine with thionyl chloride.

The *acid chloride*, prepared by warming the βγ-acid with an excess of thionyl chloride for 20 minutes and distilling the product in a good vacuum, boiled at 140°/18 mm. The αβ-isomeride boiled at 142°/18 mm. On pouring either acid chloride into water it was found that the acid produced was no longer pure, but contained 10—14% of the other isomeride, which could be separated by the copper salt process.

The *ethyl* ester prepared from the βγ-acid chloride had b. p. 143°/14 mm., $d_4^{13\cdot5°}$ 1·0285, $n_D^{13\cdot6°}$ 1·52953, $[R_L]_D$ 61·26 (calc., 59·82) (Found : C, 76·2; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). The ester gave on ozonisation a good yield of acetaldehyde, which was identified by means of β-naphthol; a trace of propiophenone was also obtained, and some acetophenone doubtless derived by hydrolysis from the benzoylacetic ester produced. The αβ-ester, prepared for comparison, had b. p. 145°/14 mm., $d_4^{13\cdot5°}$ 1·0234, $n_D^{13\cdot5°}$ 1·52827, $[R_L]_D$ 61·45, and gave propiophenone and glyoxylic acid on treatment with ozone.

Interconversion of the αβ- and βγ-acids. (1) A solution of 5 g. of either acid in 40 c.c. of 50% aqueous potassium hydroxide was boiled for a definite time. The acids were then isolated and the

* The isolation of propiophenone in this case and of butyrophenone from the higher homologue is most likely due to the admixture of a small amount of the *allo*-acid, which would not be removed in the copper salt process.

amount of conversion was estimated by the copper salt process. The results are given on p. 2749.

(2) Each acid (10 g.) was refluxed for an hour with an excess of 50% sulphuric acid. The acids were then estimated as before and the neutral products were separated by distillation in a vacuum. The low fraction consisted of *α-ethylstyrene*, b. p. 81—82°/20 mm. (Found: C, 90·7; H, 9·2. $C_{10}H_{12}$ requires C, 90·9; H, 9·1%), which on oxidation with alkaline permanganate gave propiophenone; this was identified by its semicarbazone. The high fraction, b. p. 170°/16 mm., appeared to consist of *β-phenylvalerolactone* (Found: C, 74·6; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%).

β-Propylcinnamic and β-Phenyl-Δ$^{\beta}$-hexenoic Acids.—The unsaturated ester was obtained by the phosphorus oxychloride process (see p. 2752) in 55% yield (some butyrophenone was recovered); it had b. p. 158—160°/19 mm., $d_4^{21°}$ 1·0079, $n_D^{21°}$ 1·52640, $[R_L]_D$ 66·59 (calc., 64·44).

On hydrolysis a mixture of acids was obtained which was separated into its constituents by the copper salt method; the salt of the αβ-acid is less soluble in ether than that in the ethyl series and it is necessary to extract it twice for complete separation. The αβ-acid formed needles, m. p. 96·5°, from petroleum (Found: C, 75·2; H, 7·1. Calc.: C, 75·8; H, 7·4%). The βγ-acid was a liquid (Found: C, 75·4; H, 7·4%). The structure of the acids was proved by oxidation with alkaline permanganate, the solid acid giving butyrophenone (semicarbazone, m. p. 189°) and oxalic acid, and the liquid acid propionic and benzoic acids. Both acids on dry distillation gave α-propylstyrene, b. p. 86°/14 mm., which was oxidised to butyrophenone by alkaline permanganate.

The same *anilide*, m. p. 108° (Found: N, 5·4. $C_{18}H_{19}ON$ requires N, 5·3%), was obtained from both acids by the phosphorus pentachloride method (see p. 2754). With thionyl chloride in pyridine, however, the αβ-acid gave mainly an *anilide*, m. p. 114° (Found: N, 5·3%), although some of the anilide, m. p. 108°, also was produced. The latter was the sole product from the βγ-acid, so it is presumably the βγ-compound. Both anilides gave a mixture of acids on hydrolysis.

The same *amide*, crystallising from ethyl acetate in needles, m. p. 101°, was obtained from both acids (Found: N, 7·4. $C_{12}H_{15}ON$ requires N, 7·4%) and was probably the βγ-compound, since it was produced with the aid of phosphorus pentachloride.

The *acid chlorides* were prepared as described on p. 2754; that derived from the αβ-acid had b. p. 160°/40 mm., and the βγ-isomeride boiled at 159°/40 mm. The acids regenerated from them were each found to contain 14—20% of the isomeric compound.

Heating either chloride for 3 hours gave a mixture containing 53—55% of the βγ-compound.

The *ethyl* esters were prepared from the acid chlorides and therefore were not homogeneous; the αβ-ester boiled at 161°/31 mm., the βγ-ester at 148°/16 mm. The *methyl* esters could, however, be prepared by an alternative method, namely, by the action of methyl sulphate on the sodium salts; the αβ-ester had b. p. 135°/12 mm., $d_4^{18\cdot2°}$ 1·0017, $n_D^{18\cdot2°}$ 1·52146, $[R_L]_D$ 62·10 (calc., 59·82) (Found: C, 76·4; H, 8·0. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%); the βγ-ester had b. p. 133°/12 mm., $d_4^{19\cdot3°}$ 1·0297, $n_D^{19\cdot3°}$ 1·53305, $[R_L]_D$ 61·53 (Found: C, 76·4; H, 8·0%). On oxidation with ozone the αβ-ester gave an oily ozonide, from which butyrophenone and glyoxylic acid were obtained on decomposition. The ozonide of the βγ-ester was crystalline and on decomposition gave propaldehyde, benzoylacetic acid, m. p. 104° (Found: C, 65·8; H, 4·9. Calc.: C, 65·9; H, 4·9%), and butyrophenone, the last being due to the presence of some of the αβ-isomeride in the ester used (this had been prepared through the acid chloride). The propaldehyde was identified by collecting it in well-cooled petroleum (by means of a stream of nitrogen) and passing in dry ammonia; a precipitate of the aldehyde-ammonia was then formed which deliquesced, giving the compound $C_{15}H_{19}N_3$, m. p. 74° (Waage, *Monatsh.*, 1883, **4**, 708).

The interconversion of the acids was carried out as described for the lower homologues and the results have already been given. In the experiments with sulphuric acid a *lactone*, m. p. 94—97°, b. p. 178°/14 mm., was isolated (Found: C, 75·6; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·6; H, 7·4%), and also α-propylstyrene, b. p. 86°/14 mm. (Tiffeneau, *Compt. rend.*, 1906, **143**, 650) (Found: C, 90·1; H, 9·7. Calc.: C, 90·4; H, 9·6%), which gave butyrophenone on oxidation.

allo-β-Propylcinnamic acid was prepared in the same way as the lower homologue, although in poorer yield; it melted at 86·5° and gave an amide, m. p. 101° (Stoermer, Grimm, and Laage, *loc. cit.*), which was not identical with the amide, m. p. 108°, described above.

β-iso*Propylcinnamic and* β-*Phenyl-γ-methyl-*Δ^{β}*-pentenoic Acids.*—*iso*Butyrophenone was condensed with ethyl bromoacetate in the usual way, and the benzene solution of the product treated with phosphorus oxychloride. From the mixture, half the ketone employed was recovered and the unsaturated ester, b. p. 154—160°/25 mm., $d_4^{20\cdot8°}$ 1·0158, $n_D^{20\cdot8°}$ 1·52561, $[R_L]_D$ 65·88 (calc., 64·44), isolated in 38% yield.

On hydrolysis a liquid mixture of acids was obtained in addition to a little *iso*butyrophenone. The acids were separated by the copper salt method, exactly as in the case of the propylcinnamic

acids. The *αβ-acid*, isolated in 53% yield, formed needles, m. p. 94°, from petroleum (Found: C, 75·6; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%) and gave, on oxidation with permanganate, oxalic acid and *iso*butyrophenone (*semicarbazone*, plates from alcohol, m. p. 182°. Found: N, 20·7. $C_{11}H_{15}ON_3$ requires N, 20·5%). The *βγ-acid* appeared to be present in somewhat smaller quantity (47%) and formed rosettes of needles, m. p. 95° (Found: C, 75·7; H, 7·4%). It gave benzoic and acetic acids and acetone on oxidation.

The *anilides* were prepared as described on p. 2754. The βγ-acid gave the same anilide, m. p. 121°, by both methods (Found: N, 5·4. $C_{18}H_{19}ON$ requires N, 5·3%); the αβ-acid gave small quantities of another anilide, m. p. 99° (Found: N, 5·3%), by the pyridine method and by the phosphorus pentachloride method; this is, therefore, probably the αβ-anilide.

Only one *amide*, presumably the βγ-compound, was obtained; it crystallised from ethyl acetate in needles, m. p. 113° (Found: N, 7·5. $C_{12}H_{15}ON$ requires N, 7·4%).

The *acid chlorides* boil at 153°/26 mm. (αβ) and 153°/30 mm. (βγ) respectively; they each contain 10—20% of the other isomeride. On heating for 3 hours at 140—150° a mixture is obtained containing about 55% of the βγ-compound.

The *esters* were prepared from the acid chlorides and therefore were not entirely homogeneous, although the products obtained from them on oxidation with ozone were mainly those to be expected. The αβ-esters boiled at 166°/42 mm. (methyl) and 161°/31 mm. (ethyl), the βγ- at 166°/42 mm. and 161°/33 mm. respectively.

The isomerisation of the acids was carried out as described above. In the experiments with sulphuric acid *α-iso*propylstyrene, b. p. 89°/15 mm. (Klages, *Ber.*, 1903, **36**, 3691), was isolated. This hydrocarbon was also obtained by dry distillation of either the αβ- or the βγ-acid (Found: C, 90·0; H, 9·8. Calc.: C, 90·4; H, 9·6%); it gave *iso*butyrophenone on oxidation. A *lactone*, b. p. 178°/16 mm., also was obtained.

δ-Phenyl-Δ$^{\gamma}$-penten-β-one.—This ketone was obtained in about 25% yield by the action of zinc methyl iodide on the chloride of β-methylcinnamic acid, the procedure described in Part I (J., 1923, **123**, 1361) being followed; it was isolated in the form of its *semicarbazone*, m. p. 191° (Found: N, 19·5. $C_{12}H_{15}ON_3$ requires N, 19·4%). The *ketone* regenerated from this boiled at 133—136°/12 mm.; it solidified, forming large plates, m. p. 100° (Found: C, 82·4; H, 7·6. $C_{11}H_{12}O$ requires C, 82·5; H, 7·5%).

On oxidation with ozone and subsequent decomposition the ketone gave acetophenone, but no trace of formaldehyde. Acetophenone was also obtained by treating the ketone with permanganate.

Unsuccessful attempts were made to prepare the ketone by the action of acetyl chloride on the magnesium derivative of β-bromo-α-methylstyrene (Schroeter, *Ber.*, 1907, **40**, 1594) and also by the action of α-chlorostyrene (Friedel, *Compt. rend.*, 1867, **67**, 1192) on ethyl sodioacetoacetate; in the latter case, phenylacetylene was produced.

The ketone was not affected by standing with cold sodium ethoxide for 3 days, or by boiling with 25% sulphuric acid for 2 hours; the pure semicarbazone was obtained from it in each case. An attempt was made to alkylate it by means of ethyl iodide in presence of "molecular" sodium in benzene, but although there was a vigorous reaction no ethyl derivative was isolated, the product being an oil of high boiling point. The ketone could not be condensed with ethyl sodiomalonate.

δ-Phenyl-Δ$^{\gamma}$-hexen-β-one and δ-Phenyl-Δ$^{\delta}$-hexen-β-one.—These two ketones were obtained in 20—25% yield by the action of zinc methyl iodide on the chlorides of β-ethylcinnamic acid and its βγ-isomeride respectively.

The αβ-ketone boiled at 138°/14 mm. and yielded a *semicarbazone* which formed plates, m. p. 158° (Found: N, 18·4. $C_{13}H_{17}ON_3$ requires N, 18·2%). The *ketone* was regenerated from this by means of oxalic acid (Found: C, 82·5; H, 8·2. $C_{12}H_{14}O$ requires C, 82·8; H, 8·1%). On oxidation with ozone, it gave propiophenone.

The βγ-ketone also boiled at 138°/14 mm.; it gave a *semicarbazone* which crystallised from alcohol in plates, m. p. 185° (Found: N, 18·5%). The *ketone* regenerated from this (Found: C, 82·6; H, 8·1%), on oxidation with ozone, gave acetaldehyde.

Ethylation of the two ketones. The pure ketones, on treatment in benzene solution with ethyl iodide and "molecular" sodium, gave the same ethylation product in poor yield (1 g. from 6 g. of ketone) in addition to a small quantity of initial material and a considerable quantity of high-boiling by-products. The ethylated ketone, b. p. 140—146°/14 mm., was isolated in the form of its *semicarbazone*, m. p. 174°. This, however, was not readily formed (Found: C, 69·3; H, 8·2; N, 16·3. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·1; N, 16·2%), and the quantity obtained was not sufficient for the regeneration of the ketone. A very small quantity of the new ketone was treated with cold alkaline permanganate; acetic acid was formed but no propiophenone could be detected, and therefore the ethylated ketone doubtless has the βγ-structure, CHMe:CPh·CHEt·COMe.

Interconversion of the two ketones. The two ketones, after being kept in cold alcoholic sodium ethoxide for 2 days, were isolated and each was converted into the semicarbazone, which was fraction-

ally crystallised from ethyl acetate–petroleum and then from dilute alcohol. In each case isomerisation had taken place to the extent of 25—35%. It was difficult to estimate this value exactly because the semicarbazones formed a definite mixture, m. p. 126°, which could be separated into its constituents only with great difficulty and inevitable loss (compare Kon and Linstead, *loc. cit.*).

Boiling the ketones for 2 hours with an excess of 50% sulphuric acid, or keeping them for 2 days in cold 1% alcoholic potassium hydroxide, produced 20—30% change in each case. The two isomerides, therefore, have approximately the same stability.

Attempts to condense the ketones with ethyl sodiomalonate were unsuccessful.

Condensation of Propiophenone with Acetone.—Attempts were made to prepare the two ketones described above by the direct condensation of propiophenone with acetone by the agency of sodium ethoxide; a variety of conditions was tried, such as allowing the ketones to stand with sodium ethoxide in ethereal or alcoholic solution or without a solvent; in one instance the alcoholic solution was boiled for 4½ hours. In all cases about half of the propiophenone was recovered unchanged and the required ketone, which was the αβ-compound, was formed only to the extent of 5%. High-boiling products were formed in considerable quantity in all cases, but the only definite compound isolated, b. p. 194—199°/16 mm., was obtained when the condensation was carried out in alcoholic solution. It readily gave a *semicarbazone*, m. p. 204° (Found: C, 70·4; H, 7·8; N, 15·7. $C_{16}H_{21}ON_3$ requires C, 70·9; H, 7·8; N, 15·5%). The ketone regenerated therefrom gave propiophenone on oxidation with permanganate and propiophenone and acetone on treatment with ozone and therefore may have the formula $CEtPh{:}CH{\cdot}CO{\cdot}CH{:}CMe_2$. Such a compound, however, should form a semicarbazido-semicarbazone, and this was not obtained.

Attempts were also made to condense butyrophenone and *iso*-butyrophenone with acetone, but none of the required ketones appeared to be formed. The action of zinc methyl iodide on the chlorides of the propyl- and *iso*propyl-cinnamic acids led to mixtures from which no semicarbazones or other crystalline derivatives could be isolated.

The authors' thanks are due to the Chemical Society and to the Dixon Fund of the University of London for grants to one of them (J. D. A. J.) which have defrayed the expenses of this investigation.

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SOUTH KENSINGTON. [*Received, July 15th*, 1926.]

NOTES.

The Reaction between Aluminium, Iodine, Ethyl Alcohol, and Water. Preparation of Ethyl Iodide. By A. O. Jones and G. Melling Green.

In the preparation of alkyl iodides by means of aluminium in place of the usual phosphorus, the quantities of reagents used were calculated on the basis :

$$2Al \xrightarrow{3I_2} 2AlI_3 \xrightarrow{6H_2O} 2Al(OH)_3 + 6HI \xrightarrow{6EtOH} 6EtI + 3H_2O.$$

This scheme, however, does not represent the course of the reaction, since, although this was very vigorous, it came to an end when 50% of the iodine had been transformed into ethyl iodide, and there was also a considerable evolution of a gas which forms an explosive mixture with air and may be hydrogen or a hydrocarbon. Moreover, the percentage conversion was constant even when the quantities were slightly varied. If the ethyl iodide formed was now distilled, and sulphuric acid–alcohol mixture then added, a further quantity of iodide could be distilled, becoming progressively darker in colour owing to the reaction between the hydrogen iodide formed and sulphuric acid. Substitution of phosphoric acid for the sulphuric acid gave a much smaller yield of ethyl iodide.

The research is being continued in order to prove the course of the reaction and the nature of the aluminium complex formed.

Ethyl iodide may be quickly and conveniently prepared as follows. A mixture of 25 g. of iodine, 40 c.c. of 84% (by weight) alcohol, and 3 g. of aluminium foil in small pieces is warmed gently. Once started, the reaction increases progressively in vigour, but can be controlled by cooling; it subsides in about 10 minutes, and is complete in about an hour. The product is distilled until deep red fumes appear. A cold mixture of 35 c.c. of 84% alcohol and 20 c.c. of 85% sulphuric acid is added to the cooled residue. After 15 minutes, distillation is begun, and continued until no more oily drops form in the water in the receiver. The yield of crude iodide is 13 c.c. (approx. 80%).—Technical College, Huddersfield. [*Received, June 29th*, 1926.]

The Isomeric Fluorobenzaldehydes and their Derivatives. By John Baldwin Shoesmith, Charles Edwin Sosson, and Robert Henry Slater.

Ortho- and para-fluorobenzaldehydes have now been separated from the bisulphite compounds obtained as by-products in the preparation of the corresponding fluorobenzyl bromides (Shoesmith and Slater,

this vol., p. 220). The b. p.s are : *o*-, 175°/760 mm.; *p*-, 181·5°/763 mm. (compare Rinkes, *Chem. Weekblad*, 1919, **16**, 206). *m*-Fluorobenzaldehyde could not be obtained pure in this way, but was prepared by passing a current of pure dry hydrogen for 24 hours into a commercial xylene solution of *m*-fluorobenzoyl chloride (Meyer and Hub, *Monatsh.*, 1910, **31**, 9344) of b. p. 73·4°/11 mm. in contact with palladinised barium sulphate (compare Rosenmund, *Ber.*, 1918, **51**, 591). An apparently theoretical yield of the aldehyde bisulphite compound, when dried over phosphoric oxide, became a 60% yield, the same phenomenon being noted with benzoyl chloride. m-*Fluorobenzaldehyde* is a colourless oil of b. p. 173°/760 mm. (Found : F, 14·8. C_7H_5OF requires F, 15·3%). The fluorine content was estimated by mixing 0·20 g. of the aldehyde with 0·40 g. of starch and placing small quantities of this powder and of sodium peroxide (10 g. in all were used) alternately in a Parrs bomb. The bomb was closed, well shaken, and fired in the usual way. This modification of Hahn and Reid's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1652) was necessary because the aldehyde, starch, and sodium peroxide explode spontaneously when mixed in an open vessel. The fluorine was then estimated as calcium fluoride in the usual manner.

The fluorobenzaldoximes crystallise from ligroin in fine, white plates : *o*-, m. p. 63° (Rinkes gives 62·6°) (Found : N, 10·2%); *m*-, m. p. 63° (Found : N, 10·1%); *p*-, m. p. 86·5° (Rinkes gives 81·2°) (Found : N, 10·2%).

The *fluorobenzaldehydephenylhydrazones* crystallise from aqueous alcohol in white plates : *o*-, m. p. 89·5° (Found : N, 13·2. $C_{13}H_{11}N_2F$ requires N, 13·1%); *m*-, m. p. 114° (Found : N, 13·15%); *p*-, m. p. 147° (Found : N, 13·2%).

The *fluorobenzaldehyde*-p-*nitrophenylhydrazones* crystallise from dilute acetic acid in fine, orange, rectangular needles : *o*-, m. p. 205° (Found : N, 16·3. $C_{13}H_{10}O_2N_3F$ requires N, 16·3%); *m*-, m. p. 202° (Found : N, 16·2%); *p*-, m. p. 212° (Found : N, 16·4%).

The authors gratefully acknowledge the award of a scholarship from the Carnegie Trustees to one of them (R. H. S.) and the receipt of a grant from the Earl of Moray Research Fund.—Edinburgh University. [*Received, September 9th*, 1926.]

The Oxidation of Sabinol with Hydrogen Peroxide. By George Gerald Henderson and Alexander Robertson.

This work was undertaken with the object of comparing the products of the action of hydrogen peroxide on the terpene alcohol sabinol with those formerly obtained by oxidising sabinene itself

with the same reagent. According to Semmler (*Ber.*, 1900, **33**, 1459), sabinol yields sabinylglycerol, $C_{10}H_{15}(OH)_3$, and α-tanacetonedicarboxylic acid when oxidised with potassium permanganate, but we have found that these compounds are not formed when hydrogen peroxide is used as the oxidising agent. Sabinol (b. p. 208—209°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9420, n_D 1·4874; prepared from oil of savin), in solution in glacial acetic acid, was slowly attacked by 30% aqueous hydrogen peroxide. The crude oxidation product contained a mixture of two isomeric compounds, $C_{10}H_{16}O(OH)_2$, partly free and partly in the form of acetates, which were respectively identical with the two glycol anhydrides, m. p. 172° and 174°, obtained by oxidising sabinene in a similar manner (J., 1923, **123**, 1849). The identity was proved by analysis, by determination of the mixed melting points, and by preparation of the well-defined di-*p*-nitrobenzoates. No other definite product was found except a trace of cymene.

In the paper just referred to, we stated that, although the glycol anhydrides evidently reacted with hydrogen bromide, attempts to isolate definite bromo-derivatives were not successful. The experiment has now been repeated with a larger quantity of material and under modified conditions. A solution of 3 g. of the glycol anhydride of m. p. 172° in 60 c.c. of glacial acetic acid was saturated with hydrogen bromide, kept for 3 days and then heated at 50° for ½ hour. The acetic acid and the excess of hydrogen bromide were removed in a vacuum desiccator, and the dark residue was mixed with a small quantity of alcohol; a crystalline bromo-compound was then gradually deposited. After several crystallisations from alcohol, this compound was obtained in colourless needles, m. p. 159—160° (decomp.). The quantity obtained was too small to give a satisfactory analysis, but the result indicated that the compound is probably 1 : 2 : 3 : 4-tetrabromomenthane.

The formation of the compounds $C_{10}H_{16}O(OH)_2$ from sabinol as well as from sabinene lends support to the view expressed (*loc. cit.*) that these compounds are glycol anhydrides derived from 1 : 2 : 3 : 4-tetrahydroxymenthane, which perhaps is formed as an intermediate product in the oxidation process.—UNIVERSITY OF GLASGOW.

[*Received, July 1st*, 1926.]